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This report summarizes processes for removal of radium from drinking water. Ion exchange, including strong acid and weak acid resin, is discussed. Both processes remove better than 95 percent of the radium from the water. Weak acid ion exchange does not add sodium to the water. Calcium cation exchange removes radium and can be used when hardness removal is not necessary.

Iron removal processes are discussed in relation to radium removal. Iron oxides remove much less than 20 percent of the radium from water under typical conditions. Manganese dioxide removes radium from water when competition for sorption sites and clogging of sites is reduced. Filter sand that is rinsed daily with dilute acid will remove radium from water.

Manganese dioxide coated filter sorption removes radium but more capacity would be desirable. The radium selective complexer selectively removes radium with significant capacity if iron fouling is eliminated.

Other radium removal processes that are discussed include limesoda ash softening, reverse osmosis, electrodialysis reversal and potassium permanganate-greensand filtration.

A brief discussion of process cost is given.

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REMOVAL OF RADIUM FROM DRINKING WATER

by

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

Total radium (Ra-226 plus Ra-228) exceeds the drinking water regulation maximum contaminant level of 5 pCi/L in wellwater supplies for some communities in the United States. Occurrence is most frequent in the states of Iowa, Illinois, Wisconsin, Virginia, North Carolina, Florida, Colorado and the New England States. This report is a summary of treatment processes that will remove radium from drinking water supplies. The report emphasis is on the results of four recent research projects.

Francis T. Mayo,
Director
Water Engineering Research Laboratory

ABSTRACT

This report summarizes processes for removal of radium from drinking water. Ion exchange, including strong acid and weak acid resin, is discussed. Both processes remove better than 95 percent of the radium from the water. Weak acid ion exchange does not add sodium to the water. Calcium cation exchange removes radium and can be used when hardness removal is not necessary.

Iron removal processes are discussed in relation to radium removal. Iron oxides remove much less than 20 percent of the radium from water under typical conditions. Manganese dioxide removes radium from water when competition for sorption sites and clogging of sites is reduced. Filter sand that is rinsed daily with dilute acid will remove radium from water.

Manganese dioxide coated filter sorption removes radium but more capacity would be desirable. The radium selective complexer selectively removes radium with significant capacity if iron fouling is eliminated.

Other radium removal processes that are discussed include lime-soda ash softening, reverse osmosis, electrodialysis reversal and potassium permanganate-greensand filtration.

A brief discussion of process cost is given.

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UNIT CONVERSIONS

English Units	Multiplied By	=	Metric (SI) Units
ft	0.3048		m
ft^3	28.31625		L
ft^3	0.02832		m^3
gal	3.7854		L
gal	3.785×10^{-3}		m^3
gpm	3.785		L/min
gpm/ft^2	40.7		$L/min/m^2$
in	2.54×10^{-2}		m
lb	0.454		kg
lb/ft^3	16.02		kg/m^3
MGD	3.78541		MLD
psi	70.307		g/cm^2
psi	0.0703		kg/cm^2
psi	703.07		kg/m^2

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SECTION 1

INTRODUCTION

Over the past four years the Drinking Water Research Division, Water Engineering Research Laboratory, Cincinnati, Ohio, has sponsored four cooperative agreements to perform research on the removal of radium from drinking water sources. These cooperative agreements were with the University of Illinois, University of Iowa, North Carolina State University and the Redhill Forest Property Owner's Association in Colorado. Ion exchange, iron and manganese removal, and sorption onto manganese dioxide coated acrylic filters were investigated under the first three projects. Iron and manganese, ion exchange and Dow Chemical Company's radium selective complexer (used for waste brine) were investigated full scale, at the small community of Redhill Forest. Most of this report will be devoted to summarizing the results of these cooperative agreements.

Other processes that remove radium are lime softening, reverse osmosis, and electrodialysis. Results from the literature showing the effectiveness of these processes are also included in this report.

The potassium permanganate greensand filtration process has been shown to remove radium but the mechanisms for removal have never been determined. Some data showing radium removal across the greensand process is included in this report.

The radium selective complexer was investigated on waste brine under one of the cooperative agreements mentioned above, and these data along with some of Dow Chemical's results on the radium selective complexer are discussed.

SECTION 2.

RESULTS AND CONCLUSIONS

ION EXCHANGE

Studies conducted at the University of Illinois yielded the following results:

1. Strong acid ion exchange resin in the sodium or hydrogen form removed 99 percent of the radium and/or barium from the water when the resin was regenerated with 4.72 meq (NaCl or HCl)/g dry resin. This is typical for softening applications. At steady state conditions, both radium and barium were being removed to concentrations much lower than their maximum contaminant levels (MCL's) when hardness started to break through at 215 bed volumes (BV). This water had hardness, barium and radium concentrations of 200 mg/L as $CaCO_3$, 20 mg/L and 20 pCi/L respectively. The strong acid resin has less capacity for radium and barium on water with higher hardness and more capacity for radium and barium on water with lower hardness.
2. Strong acid resins have the following preference: $Ra^{2+} > Ba^{2+} > Ca^{2+} > Mg^{2+} > Na^{+}$. Because of the selectivity radium and barium were much more difficult to remove from the resin during regeneration than calcium and magnesium. Economical regeneration removes most of the hardness ions, but radium and barium buildup on the resin after repeated cycles to the point where equilibrium is reached and then radium and barium will begin to breakthrough shortly after hardness.
3. Regeneration of the sodium form strong acid resin for water with 200 mg/L ($CaCO_3$) hardness with application of 6.5 lb $NaCl/ft^3$

(4.72 meq/g) resin produced 2.4 BV of 16,400 TDS brine per 100 BV of product water. If all of the radium and barium were removed from the product water, then the brine would contain radium and barium concentrations that equal the raw water concentration times 100/2.4. This assumes that the 2.4 BV of brine includes the concentrated brine and final rinse.

4. Strong acid resins in the hydrogen form would not normally be used for drinking water treatment because of the resulting strong mineral acids that would form in the product water.

5. Weak acid ion exchange resins only remove cations that are balanced equivalently with alkalinity; they must be regenerated with a strong acid such as hydrochloric or sulfuric and they exchange hydrogen ions for divalent cations, thereby forming carbon dioxide which must be removed by stripping. The sodium concentration in the drinking water will not increase when weak acid resins are used unless a chemical such as Na_2CO_3 were added to increase alkalinity.

6. The weak acid ion exchange resin removed greater than 95 percent of the radium and/or barium when the resin was regenerated with 8.5 meq HCl/g dry resin. The regenerant dose of 8.5 meq HCl/g dry resin yielded a regeneration efficiency of 93 to 96 percent and a column utilization of 70 percent which is very close to the optimum operating condition. At the above steady state conditions both radium and barium were being removed to concentrations much lower than their MCL's and barium began to break through at 650 BV's which was a little later than hardness. Radium continued to be removed after hardness break through but

the exact break through point for radium was not determined. These tests were performed on water with hardness and alkalinity concentrations of approximately 200 and 250 mg/L as $CaCO_3$ respectively. Radium and barium concentrations were approximately 20 pCi/L and 20 mg/L respectively.

7. Weak acid resins have the following preference: $Ra^{2+} > Ba^{2+} > Ca^{2+} > Mg^{2+} > H^+$. The weak acid resin was easier to regenerate than the strong acid resin and therefore a smaller quantity of brine will be required per unit of water treated. The weak acid resin comes to equilibrium after fewer cycles than for the strong acid resin because cations including radium and barium are much easier to remove from the resin during regeneration.

8. Regeneration of the weak acid resin, for water with 200 and 250 mg/L as $CaCO_3$ hardness and alkalinity respectively at a regenerant dose of 8.5 meq HCl/g dry resin, produced 1.2 BV of spent brine with a TDS of 19,900 mg/L per 100 BV of product water. If all of the radium and barium were removed from the product water, then the brine would contain radium and barium concentrations that equal the raw water concentration times 100/1.2. This assumes that the 1.2 BV of brine includes the concentrated brine and final rinse.

9. The cost of using a weak acid resin is greater than that of the strong acid resin by about $0.15/1000 gal and $0.08/1000 for a 0.1-MGD and 1-MGD plant respectively. The use of a strong acid resin costs approximately $1.36/1000 gal and 0.38/1000 gal for a 0.1-MGD and 1-MGD plant respectively.

10. Strong acid resin in the calcium form can be used to remove radium and barium. The process would be useful for low hardness waters that exceed the radium MCL. Calcium cation exchange can also be used to remove radium from the by-pass water for conventional ion exchange plants.

IRON AND MANGANESE REMOVAL

The University of Iowa study yielded the following results:

1. Sorption of radium onto iron oxides increases as pH and iron concentration increase, but typical pH values and iron concentrations for natural waters are too low for significant radium removal in the presence of other competing cations. Sorption of radium to existing iron oxides in natural waters is expected to be less than 20%.
2. The amount of radium sorbed onto iron flocs decreased as the concentration of divalent cations, such as barium, calcium and magnesium increased.
3. A series of experiments that compared radium sorption onto natural iron oxides with that onto synthetic iron oxides showed no difference between the two.
4. Tests in sodium synthetic water showed that sorption of radium onto the iron oxide surface takes place and not incorporation of radium into the ferrous ion as oxidation is taking place. This was shown by adding radium in the presence of ferrous ion before aeration and then adding radium after the iron was oxidized. The same quantity of radium (75%) was removed in both cases.
5. Radium removals by freshly precipitated hydrous manganese oxides were much greater than removal by iron oxides.

6. Radium sorption onto 1 mg/L MnO_2 increased from 80 to 90 percent as pH increased from 6.5 to 9. This was in synthetic water containing 300 mg/L calcium as $CaCO_3$. The higher sorptive capacity of manganese dioxide over iron oxides is based on the lower point of zero charge for MnO_2 in water which takes place at pH less than 5. Therefore, MnO_2 has good sorptive capacities over the normal pH range of natural waters.

7. The addition of 5 mg/L pure MnO_2 to Oxford water (hardness = 1300 mg/L as $CaCO_3$) removed 90 percent of the radium at pH 7. Iron was oxidized and removed prior to MnO_2 addition.

8. Sorption to MnO_2 appears to be a good radium removal mechanism if sorption of ferrous ion and coating of the manganese oxides with iron oxides can be eliminated.

9. Filter sand has a potential capacity to sorb radium at typical hardness concentrations if the capacity is maintained by periodically rinsing the sand with a dilute acid. Removal efficiencies of approximately 80 to 90 percent were achieved in laboratory and pilot plant studies when daily rinsing with a dilute acid (0.1 to 0.01N) was practiced. The raw water radium concentration was approximately 50 pCi/L.

10. Radium sorption to filter sand is not very sensitive to normal pH variation encountered in drinking water (pH 6.5 to 8.5).

11. During laboratory jar tests, percent radium sorption increased as sand concentration increased, but sorption was not a function of radium concentration.

12. Pilot scale field studies at Oxford, Iowa (Hardness = 1300 mg/L as $CaCO_3$), on water with iron removed, showed that sand reduced

radium from approximately 10 to 1 pCi/L. The sand filter was regenerated once a day with 0.1 N HCl and the loading rate was 1.5 gpm/ft^2.

13. Pilot scale field studies at Oxford, Iowa, on water that contained 0.5 mg/L iron and iron floc, showed that sand only removed 25 to 35% of the radium. This sand filter was also regenerated once a day with 0.1 N HCL and the loading rate was 1.5 and 3.0 gpm/ft^2.

MANGANESE DIOXIDE COATED FILTERS

The North Carolina State University study yielded the following results:

1. A process was developed for coating MnO_2 onto woven acrylic cartridge filters. Hot $KMnO_4$ solution is circulated through the filter and the investigator explains that $KMnO_4$ is reduced by oxidizing the acrylic filter material resulting in MnO_2 that adheres to the filter. A 10-inch long, 250 gram filter contains 56.25 grams MnO_2 or 22.5 percent MnO_2 by weight.
2. On high hardness water, a ten-inch MnO_2 filter treated 800 ft^3 of water before the effluent radium concentration exceeded 5 pCi/L. The influent had a radium concentration of 36 pCi/L, hardness concentration of 227 mg/L, as $CaCO_3$, iron and manganese concentration that was insignificant and a pH of 7.8.
3. On low hardness water, a ten-inch MnO_2 filter treated 1000 ft^3 of water before the effluent radium concentration exceeded 5 pCi/L. The influent had a radium concentration of 13 pCi/L, hardness concentration of 23 mg/L as $CaCO_3$, iron and manganese concentrations that were insignificant and a pH of 4.5.

4. If a radium removal plant were built using ten-inch MnO_2 filters and each filter treated water at a rate of 1 gpm for 7500 gallons (1000 ft^3), then the filters would have to be changed every 5.2 days for the plant to stay in compliance with the radium MCL. It would be unrealistic to change radioactive filters, that require special handling, this often, and therefore, I conclude that MnO_2 filters are impractical for radium removal unless they can be developed to have much greater capacity. The final project report on MnO_2 filters is still being prepared and the investigators may have a different opinion.
5. Data from this study also showed that MnO_2 has significant capacity for sorption of other metals including iron and manganese ions. This agrees with the University of Iowa study.

EVALUATION OF RADIUM REMOVAL AND WASTE DISPOSAL FOR SMALL COMMUNITY WATER SUPPLY

The study by Rocky Mountain Consultants at Hartsel, Colorado yielded the following results:

1. Results showed that very little radium is removed across the iron removal process which agrees with the Univeristy of Iowa study.
2. Ion exchange removed radium to concentrations below the MCL and hardness broke through before radium. Radium broke through between 134 and 179 bed volumes of treated water. Hardness concentration in the source water was approximately 265 mg/L as $CaCO_3$.
3. Greater than 99% of the radium (influent radium concentration was approximately 1230 pCi/L) was removed from the waste brine

by the RSC. The RSC has treated over 1023 BV of waste brine without radium breakthrough. The RSC is truly radium selective because the influent and effluent TDS concentrations were approximately the same at 42,000 mg/L. These conclusions are not final because the project will not be completed until October, 1987.

OTHER RADIUM REMOVAL PROCESSES

Results obtained from various studies cited in the literature yielded the following conclusions:

1. Lime and lime soda softening have been demonstrated on a full-scale plant level to achieve 75 to 96% removal of radium.
2. Data indicate that radium removal, for the lime and lime soda softening processes is pH dependent with 84 percent and 94 percent radium removals at pH 9.5 and 10.5 respectively.
3. The radium selective complexer selectively removed radium from drinking water to concentrations below the MCL for extended lengths of time as long as iron fouling was eliminated. Best results were for a pilot demonstration in Washington, Iowa where the RSC removed greater than 90 percent of the radium for eleven months. Iron and manganese were not a problem at this location.
4. Low pressure (<200 psi) reverse osmosis membranes will remove greater than 95 percent of the divalent cations including radium. High pressure reverse osmosis units that are well maintained will give better than 98% radium removal.
5. Electrodialysis reversal (EDR) removes about 40 percent of the dissolved solids, including radium, per stage. Ion profile, ion concentration and water temperature affect radium removal and therefore EDR stage configuration should be arranged for

specific waters on which they are used.

6. Good radium removal for some iron removal plants using $KMnO_4$ - Greensand filtration has been reported. In my opinion, a properly designed $KMnO_4$ - filtration system should remove radium. Ferrous ion and iron floc must be removed first so they will not compete with radium or clog sorption sites. About 1 mg/L of MnO_2 formed by the stoichiometric addition of Mn^{2+} and $KMnO_4$ should be all that is needed.

COSTS DISCUSSION

The water analysis for specific water supplies will determine the type of treatment plant that is required and, therefore, cost. For example, if the water needs radium removal and softening, then ion exchange or lime soda softening would be required. If the water is brackish, then reverse osmosis or electrodialysis reversal would be used and so forth. Some locations may require both iron removal and softening. If the water only requires radium removal, then the RSC, $KMnO_4$-filtration or calcium cation exchange would probably be used. Approximate costs for the different treatment processes that remove radium were taken from the literature and tabulated in this report.

SECTION 3.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. Weak acid ion exchange resins should be tested in the laboratory for radium removal at a few alkalinities that are equivalently less than hardness. Weak acid ion exchange resins should be pilot tested for radium removal at two locations on waters of lower equivalent alkalinity than hardness. The two locations could have alkalinities that are equivalently equal to 1/3 and 2/3 of the hardness.
2. Calcium cation exchange has very good potential for removing radium and not hardness and, therefore, this process should be pilot tested for radium removal on waters where hardness removal is not desired.
3. Potassium permanganate - filtration should be studied in the laboratory and pilot tested for radium removal.
4. Sand should be studied in the laboratory to determine optimum conditions for radium removal.
5. Electrodialysis should be pilot tested on a brackish drinking water supply to determine radium removal efficiency and cost.
6. The radium selective complexer should be studied in the laboratory to determine capacity for radium at low through high TDS concentrations. A cost comparison should be made for the RSC, when used on influent vs. waste brine. Methods for disposal of the RSC should be investigated.
7. A cost study should be performed comparing radium removal with calcium cation exchange, $KMnO_4$-filtration and the RSC.

8. A paper study should be made to determine when water treatment waste containing radium is a problem. Economical ways to handle this waste should be determined.

SECTION 4.

ION EXCHANGE

(University of Illinois Study)[1]

SUMMARY OF ION EXCHANGE

A study was completed at the University of Illinois to develop technology that can be used by small water treatment plants to remove hardness, barium, and radium. Special emphasis was placed on finding an alternative to strong acid ion exchange (which is used in the sodium (Na^+) form) because of the large amounts of Na^+ this process adds to treated water. The primary objective of this study was to determine the applicability of weak acid exchange resin (in the hydrogen (H^+) form) for removal of hardness, barium, and radium from the types of groundwater encountered in northern Illinois. Ion exchange is particularly suited to small communities where hardness, barium, and/or radium may be a problem. The capacity of the weak acid ion exchange resin and the regeneration requirements were determined and compared with those of strong acid resins for the same application.

The strong acid resin in the sodium form was tested with an influent water containing approximately 200 mg/L as calcium carbonate ($CaCO_3$) hardness, 250 mg/L as $CaCO_3$ total alkalinity, 20 mg/L barium (Ba^{2+}) and 20 picocuries/liter radium-226 (pCi/L Ra-226). The optimum regenerant dose was found to be 6.5 lb sodium chloride (NaCl)/ft^3 (4.72 meq/g dry resin), which is typical for softening applications. Application through several exhaustion/regeneration cycles led to steady-state performance; approximately 215 bed volumes (BV) of water was applied before hardness breakthrough, and both Ba^{2+} and Ra-226 were removed to concentrations much lower than their maximum contaminant levels (MCL's). Ba^{2+} broke through together with the hardness, and, at a hardness concentration of 40 mg/L (at 225 BV), the 1-mg/L MCL for Ba^{2+} had been exceeded. Radium-226 removal to less than the MCL of 5 pCi/L continued even after the resin was completely saturated with hardness. The regeneration efficiency (equivalents of metal ions removed per equivalent of NaCl applied) was about 60%, column utilization (percent of maximum capacity used per exhaustion cycle) was 60%, and 2.4 BV of 16,400 TDS brine was produced per 100 BV of product water.

The weak acid resin in the hydrogen form was tested as an alternative to the strong acid resin because the latter greatly increases the amount of Na^+ in the product water. The weak acid resin has a much higher total capacity (11.5 meq/g versus 4.8 meq/g) than the strong acid resin. The weak acid resin must be followed by CO_2 stripping and pH adjustment, and the resin does swell significantly as it is converted from the H^+ form. Also the weak acid resin will only remove cations that are matched by equal equivalents of alkalinity. Application of the same water used to test the strong acid resin was used for several cycles of exhaustion-regeneration to observe steady-state behavior. Both Ra-226 and Ba^{2+} were removed to levels far below the MCL's, and Ba^{2+} broke through about the same time as the hardness, after about 600 BV of product water had been processed. Radium-226 continued to be removed even after the resin was saturated with hardness. The regenerant dose of 8.5 meq HCl/g dry resin yielded a column utilization of 70%, a regeneration efficiency of 93 to 96%, and 1.2 BV of spent brine with a TDS of 19,900 mg/L per 100 BV of product water.

The cost of using the weak acid resin with HCl regenerant was somewhat higher than that for using the strong acid resin in the Na^+

form. For example, the use of a strong acid resin costs approximately \$1.36/1000 gal for a 0.1-MGD plant and \$0.38/1000 gal for a 1-MGD system. The use of a weak acid resin will increase these costs by \$0.15/1000 gal and \$0.08/1000 gal, respectively.

In addition to the above, a strong acid resin in the calcium form was found to effectively remove Ba^{2+} and Ra^{2+} to concentrations below the MCL. The calcium form resin does not add sodium to the water and it would be useful for situations where hardness removal is not desired.

The following is a more detailed discussion of the University of Illinois study.

RESULTS AND DISCUSSION

Definition of Column Utilization and Regeneration Efficiency

The terms column utilization and regeneration efficiency will be used in the following discussion on strong and weak acid resins and, therefore, the definitions of these terms is given here.

$$\%\ \text{Column Utilization} = \frac{\text{breakthrough capacity (meq/g)}}{\text{maximum capacity (meq/g)}} \times 100 \qquad (1)$$

where:

Breakthrough Capacity = total equivalents of metal ions removed from the water during the service cycle per gram of resin

Maximum Capacity = maximum capacity of the resin as stated by the manufacturer in equivalents/gram of resin. (11.5 meq/g for Diolite C-433) (4.9 meq/g for Diolite C-20)

$$\text{Regeneration Efficiency} = \frac{\text{total equivalents of metal ions removed during regeneration}}{\text{total equivalents of ions applied during regeneration}} \times 100 \qquad (2)$$

Strong Acid Resins

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The strong acid resin is usually used in the sodium form and involves a stoichiometric exhaustion as shown in reaction (3).

Service:

$$2Na^+ R^- + X^{2+} + 2A^- \dashrightarrow X^{2+}R_2^- + 2Na^+ + 2A^- \qquad (3)$$

Regenerate:

$$X^{2+} R_2^- + 2NaCl \dashrightarrow 2Na^+ R^- + X^{2+} + 2\ Cl^- \qquad (4)$$

where: R = resin

X = Ra, Ba, Ca, Mg

A = HCO_3, Cl, 1/2 SO_4

Regeneration of the resin is the reverse of the exhaustion process and an excess of regenerant is required to force the reverse reaction (4) to take place because the reactions are favorable in the direction shown in reaction (3).

The capacity of strong acid resins depends upon the number of functional groups on the resin and also upon the amount of regenerant applied. If low regenerant doses are used, a lower capacity will result[2] because some resin sites are not converted back to the Na^+ form. Table 1 shows that smaller amounts of NaCl remove more cations per unit of NaCl added (higher regeneration efficiency). However, smaller amounts of NaCl used during regeneration result in a lower resin capacity (column utilization) that can be used for hardness, barium and radium removal.

TABLE 1. EFFICIENCY AND COLUMN UTILIZATION AS A FUNCTION OF REGENERATION LEVEL, Na^+-FORM[3]

Regeneration Level ($lb\ NaCl/ft^3$ resin)	Hardness Removed ($lb\ CaCO_3/ft^3$ resin) Theoretical	Actual	Regeneration Efficiency (%)	Column Utilization (%)
1	0.85	0.83	98	14
2	1.70	1.32	78	22
3	2.55	1.83	72	30
5	4.25	2.85	67	47
10	8.50	3.90	46	64
15	12.75	4.65	36	76
20	17.00	5.00	29	82

A strong acid resin, Duolite C-20 manufactured by Diamond Shamrock* was used and Table 2 gives the characteristics of this resin.

TABLE 2. STRONG ACID RESIN CHARACTERISTICS

	C-20
Matrix	Polystyrene
Crosslinking	Divinylbenzene
Functional Group	Sulfonate
Capacity	4.9 meq/g
Mesh Size	16 x 50
pH Range	0 - 14

Steady State Condition (strong acid resin) --

Repeat runs were made using C-20 resin to determine barium and radium removal at steady state conditions. Test water had the analysis given in Table 3. The result of repeat runs for the strong acid resin is shown in Figure 1. Figure 1 gives effluent barium concentrations when the effluent hardness concentration had broken through at 40 mg/L as $CaCO_3$. The figure shows that there was essentially no difference between the hydrogen and sodium form resin for barium breakthrough as

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*Now Rohn and Haas Co.

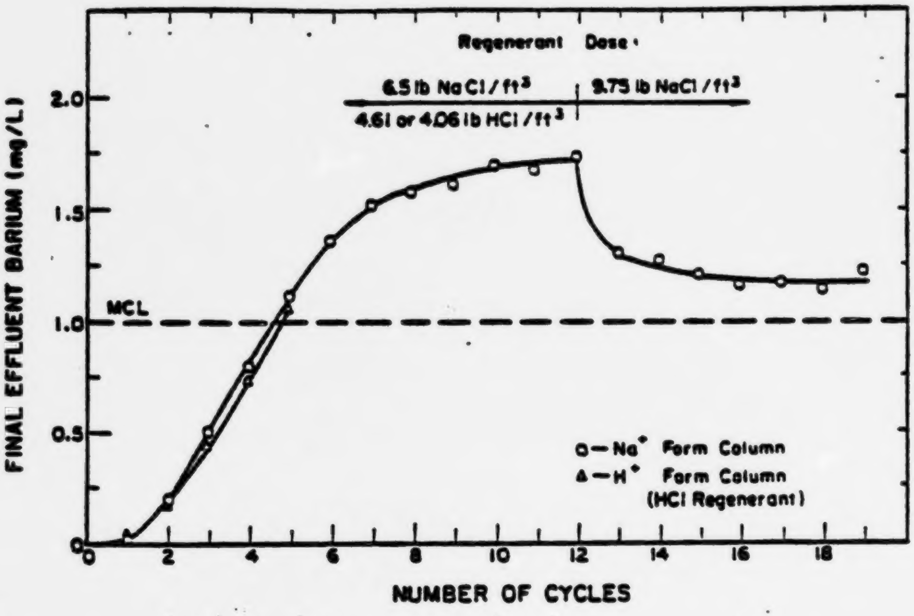

Figure 1. Barium effluent concentration from strong acid resin exhaustion-regeneration cyclic studies. The barium values shown are those when the effluent hardness concentration is 40 mg/L as $CaCO_3$.

TABLE 3. TEST WATER ANALYSIS FOR STRONG ACID RESIN RUNS

Parameter	Concentration
Na (mg/L)	38.7
Mg (mg/L as $CaCO_3$)	102.2
Ca (mg/L as $CaCO_3$)	102.2
Ba (mg/L)	19.8
Ra-226 (pCi/L)	19.1
Total Hardness (mg/L as $CaCO_3$)	204.4
Total Alkalinity (mg/L as $CaCO_3$)	251.5
pH	6.5-7.2

shown for duplicate tests for the first five cycles. A NaCl application of 6.5 lb/ft^3 of resin contains 4.72 meq/g of resin the same as 4.06 lb HCl/ ft^3. These results indicate that there was essentially no difference in the regeneration efficiencies between NaCl and HCl solutions when equal equivalents of each regenerant were used. The effluent barium concentration leveled off at 1.7 to 1.75 mg/L for the cycles when 6.5 lb of NaCl/ft^3 of resin was used for regeneration of the sodium from resin column. The effluent barium concentration dropped to about 1.2 mg/L at the end of each cycle after the regenerant dose was increased by 50% to 9.75 lb NaCl/ft^3 of resin. By the 19th cycle, 0.86 meq of Ba^{2+}/g was on the resin before regeneration and 0.62 meq/g remained after regeneration.

The results shown in Figure 1 indicate that barium (and hence also radium) does accumulate on the strong acid resin with successive exhaustion-regeneration cycles. This accumulation levels off at a concentration dependent on the total hardness concentration at which the run is terminated, and on the amount of regenerant applied for each regeneration. In the 10th and 11th cycles of the sodium form of the resin, for example, the divalent cation removal was 2.77 meq/g resin, which is about 58% of the maximum capacity of the resin. A large portion of the remaining 42% of the maximum capacity was occupied by ions that were not removed by the regenerant.

The regeneration efficiency (equivalents removed per equivalent of regenerant applied), obtained for the 10th and 11th cycles with 6.50 lb $NaCl/ft^3$ of resin was 58 to 59%. The average TDS of the 2.4 BV of waste brine produced per 100 BV of product water was 16,400 mg/L. The waste brine figure does not include the backwash water which would be used to backwash the resin beds for each regeneration but does include the rinse water. No effort was made to minimize the volume of brine produced.

The regeneration efficienty obtained for the 17th, 18th, and 19th cycles (see figure 1), with application of 9.75 lb $NaCl/ft^3$ of resin, was 46.0%. The waste brine produced was 2.07 BV per 100 BVs of product water; the average TDS of the brine was 25,200 mg/L. The capacity used during these cycles was 3.26 meq/g for a column utilization of 67.9%.

The breakthrough curves shown in Figure 2 were determined during the 6th exhaustion of the sodium form resin column, with 6.50 lb $NaCl/ft^3$ of resin applied as regenerant. The leakage of barium during most of the cycles was very low, approximately 0.10 mg/L, including at the beginning of the run. Very low total hardness leakage was also observed for this cycle. Barium and total hardness broke through together at approximately 225 BV. Effluent samples taken during the 9th, 10th, and 11th cycles of this column continued to show leakage of less than about 0.15 mg/L of barium during most of each cycle.

The breakthrough curves determined during the 19th cycle of the sodium form resin column, with a regenerant dose of 9.75 lb $NaCl/ft^3$ of resin, were very similar to those shown in Figure 2. The leakage of

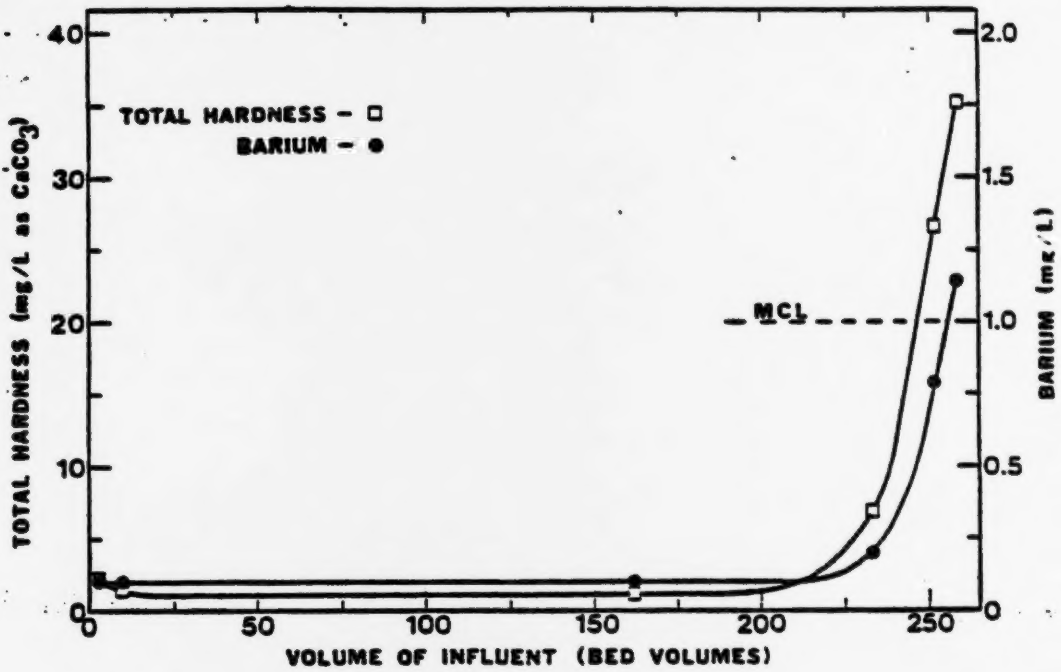

Figure 2. Breakthrough curves for the sixth exhaustion cycle of the strong acid resin.

barium was between 0.10 mg/L and 0.20 mg/L for the entire run. Hardness and barium did breakthrough somewhat later at 260 to 270 BV, however, in keeping with the usage of a higher percentage of the resin capacity.

The leakage shown in Figure 2 indicates that the barium remaining on the resin after the completion of the regeneration/rinse portion of the cycle is tightly held by the resin. The barium is not easily displaced by the high concentration of Na^+ released in the subsequent saturation cycle as hardness is removed from the influent.

Regeneration (strong acid resin) --

The regeneration of each column was performed upflow, countercurrent to the direction of flow during the exhaustion run. The resin remained firmly packed in the columns at all times, however. Effluent samples were taken continuously throughout regeneration and analyzed for magnesium, calcium, and barium; the HCl regeneration curves for the acid form of the resin are shown in Figure 3. The curves show the cumulative metal ion removal as a function of the amount of regenerant applied. Calcium and magnesium are removed most effectively during the first portion of the regeneration. At a regenerant dose equivalent to the resin capacity (at line A), 55% of all ions were removed (based on the total amount eventually removed from the resin during regeneration), 80% of the magnesium and 67% of the calcium were removed. Barium was the most difficult ion to remove. Only 15% of the barium ions were removed by this amount of regenerant. After an amount of regenerant equal to three times the equivalents of divalent cations removed (line C) was applied, essentially all of the calcium and magnesium were removed from the resin - but more than 50% of the barium remained on the resin.

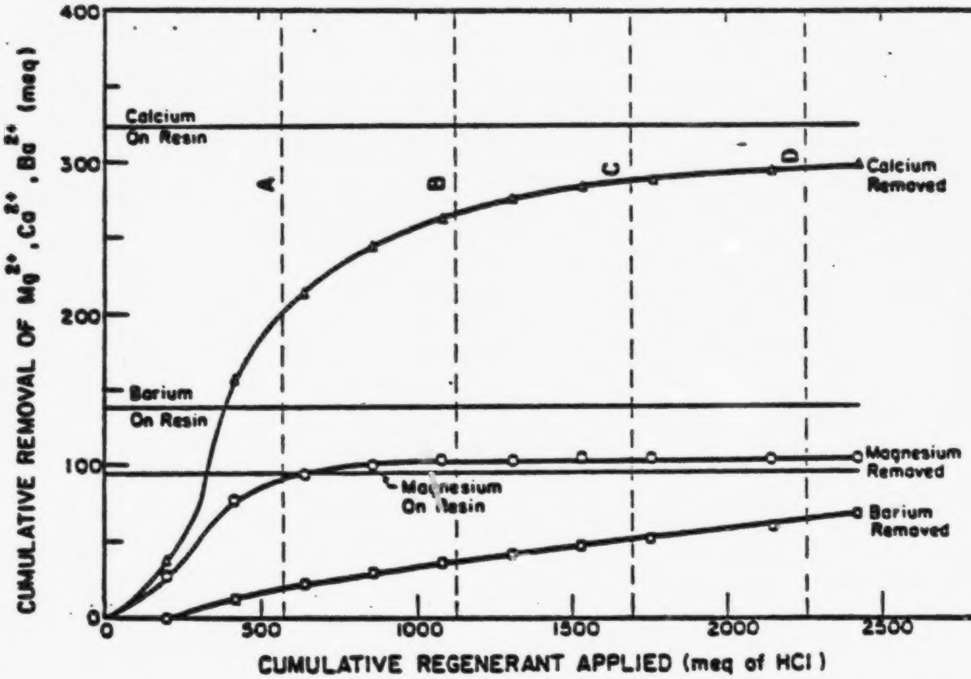

Figure 3. Acid regeneration of virgin strong acid resin (2). At A, B, C and D, respectively, the amount of regenerant applied is 1, 2, 3 and 4 times the number of equivalents of cations removed by the resin.

The regeneration curves for the sodium chloride regeneration of the column originally in the salt form are very similar to those obtained for the hydrochloric acid regeneration and thus they are not shown. No difference in the regeneration ability of the hydrochloric acid versus sodium chloride was observed.

A large regenerant dose would be required to regain the full capacity of this strong acid resin. In municipal softening operations resin capacity is often sacrificed in order to achieve greater regeneration efficiency.[2] Municipalities often operate with a regenerant dose of approximately the capacity of the resin (or the equivalents of divalent ions on the resin) where about 50% removal of the ions is obtained according to the results shown in Figure 3. The capacity of the resin available in a subsequent production run is then limited by cations still present on the resin. The results from two virgin resin column studies also indicate that with only partial regeneration of a resin bed between service runs, as in a municipal softening application, barium will accumulate on the resin. This condition is expected to alter the relative amount of water that can be processed before hardness and barium breakthrough.

Radium Removal (strong acid resin) --

Table 4 gives the results of a test for radium removal using virgin strong acid resin in the hydrogen form. Influent Ra-226 averaged 18.5 pCi/L for this test. Table 4 gives effluent Ra-226 concentrations along with total hardness, barium, and sodium concentrations in the effluent samples. The data show that Ra-226 removal continued long after the saturation of the column with hardness ions.

TABLE 4. RADIUM REMOVAL, SECOND STRONG ACID VIRGIN RESIN COLUMN TEST
(Influent Ra-226 average = 18.5 pCi/L)

Influent Applied (BV)	Effluent ^{226}Ra (pCi/L)	Effluent Na^+ (mg/L)	Effluent Hardness (mg/L as $CaCO_3$)	Effluent Ba^{2+} (mg/L)
25	1.4	0	0	0
380	2.1	112	0	0
881	2.3	36	214	0
1121	2.0	46	200	0
1622	2.7	47	201	1.0

These samples were analyzed in the Environmental Research Laboratory, University of Illinois, Urbana, IL.

Influent, effluent, and regeneration samples from several cycles of the steady state sodium form resin column test were analyzed for radium-226. Using one liter samples and the radon emanation technique, the detection limit for Ra-226 is 0.1 pCi/L. The regenerant dose (shown in Figure 1) was 6.5 lb $NaCl/ft^3$ of resin for runs 1 through 11 and 9.75 lb $NaCl/ft^3$ of resin for runs 12 through 19. Results are given in table 5. Excellent radium removal by the column was observed for each of the runs. After the 11 cycles at the lower regenerant dose, the column still produced product water with an average radium-226 concentration of 0.1 pCi/L. After eight additional cycles of the column at the higher regenerant dose, the average radium-226 concentration in the product water was below 0.1 pCi/L. Throughout each cycle the radium-226 concentration in the effluent was quite low, and at no point did the concentration exceed the MCL of 5 pCi/L. After comparing the data in table 5 to the data in table 4 and figure 1 at approximately the same hardness breakthrough, one can conclude that the strong acid resin perfers radium over barium and preference of the strong acid resin for cations is Ra > Ba > Ca > Mg > Na.

TABLE 5. RADIUM REMOVAL, STRONG ACID RESIN CYCLIC TESTS

	Influent Applied (BV)	Radium-226 (pCi/L)	Total Hardness (mg/L as $CaCO_3$)
Cycle No. 1			
Influent		19.1	195
Point Effluent	420	0.3	39
Average Effluent	425	0.1	2.3
Cycle No. 4			
Influent		8.4	209
Point Effluent	8	0.3	1.1
Point Effluent	264	0.2	43
Average Effluent	270		2.6
Cycle No. 6			
Influent		17.7	199
Point Effluent	6	<0.1	1.7
Point Effluent	164	0.3	1.2
Point Effluent	254	0.3	30
Average Effluent	259	<0.1	1.6
Cycle No. 11			
Influent		18.2	216
Point Effluent	27	<0.1	0.8
Point Effluent	182	<0.1	0.8
Point Effluent	248	3.0	23
Average Effluent	255	0.1	1.7
Cycle No. 19			
Influent		18.4	200
Point Effluent	5	0.2	0.4
Point Effluent	216	<0.1	0.4
Point Effluent	261	0.1	4.6
Point Effluent	287	0.7	26
Average Effluent	295	<0.1	1.6

Cycles 6 through 11 were analyzed in the Environmental Research Laboratory, University of Illinois, and cycles 1 through 4 were analyzed in the University Hygienic Laboratory, University of Iowa.

Table 6 shows the amount of radium-226 removed by column regeneration. An accumulation of radium-226 on the resin was observed, but the accumulation per cycle decreased with each successive cycle. After 11 cycles at a regenerant dose of 6.5 lb NaCl/ft^3 of resin, almost 85% of the radium-226 adsorbed during the 11th cycle was removed. After eight additional cycles at a regenerant dose of 9.75 lb NaCl/ft^3 of resin, close to 95% of the radium adsorbed during the 19th (and last) cycle was removed by regeneration. Hence radium accumulates on the resin but eventually comes to equilibrium where all of the radium adsorbed will be removed during regeneration (assuming that the length of service and quantity of regenerant remain constant).

The small accumulation of radium-226 on the column will not affect resin capacity. During the entire 19 runs of the cyclic test, 29,800 pCi of radium-226 was passed through the column. Even if all of the radium accumulated, only 2.7 x 10^{-7} meq of radium would be on the column; a negligible amount when considering the resin capacity of approximately 5.0 meq/g.

TABLE 6. RADIUM ACCUMULATION, STRONG ACID RESIN CYCLIC TESTS

Run No.	Waste Brine ^{226}Ra (pCi/L)	Waste Brine Produced (BV/100 BV Product Water)	Percent ^{226}Ra Removed During Regeneration
4	274	2.30	
6	418	2.37	56.0
11	639	2.41	84.8
19	846	2.05	94.4

Weak Acid Resins

Weak acid resins remove only cations that are balanced with alkalinity and involve stoichiometric exhaustion as shown in reaction (5).

Service:

$$2H^+R^- + X^{2+} + 2HCO_3^- \rightarrow X^{2+} R_2^- + 2CO_2(aq) + 2H_2O \qquad (5)$$

Regeneration:

$$X^{2+}R_2^- + 2HCl \rightarrow 2H^+R^- + X^{2+} + 2Cl^- \qquad (6)$$

where: R = resin
X = Ra, Ba, Ca, Mg

Regeneration takes place as shown by reaction (6). Regeneration for weak acid resins is very efficient and requires only about ten percent above stoichiometric excess regenerant. Regeneration requires application of a strong acid such as hydrochloric or sulfuric. Sulfuric acid is less expensive than hydrochloric acid but regenerating with sulfuric acid could cause $CaSO_4$ precipitation within the resin. Therefore, the most economical regenerant would be a mixture of dilute hydrochloric and sulfuric acids to eliminate $CaSO_4$ precipitation. Sulfuric acid should not be used for regeneration if barium is present because of the possibility of $BaSO_4$ precipitation in the resin.

Carbon dioxide, produced during the service cycle, must be removed by stripping. Reaction (5) will not go to the right unless alkalinity is present because pH of the solution drops below 4.5, if alkalinity is not present, and the concentration of H^+ becomes large enough to cause the release of divalent ions from the resin according to reaction (6). The addition of a small quantity of Na_2CO_3 is possible to increase alkalinity if enough natural alkalinity is not present for the desired divalent cation removal.

Some of the advantages of the weak acid resin include ease of regeneration and the consequential smaller quantity of brine per unit of water treated. Downing[4] obtained the best regeneration with 1 to 4 percent HCl solutions. If H_2SO_4 is used, lower concentrations should be used to eliminate the possibility of $CaSO_4$ or $BaSO_4$ precipitation in the resin bed. Dow Chemical U.S.A. (1977) suggests using 0.119 lb of 100 percent H_2SO_4/eq capacity utilized as a 0.5 to 1 percent H_2SO_4 solution, but they did not address the concentration of H_2SO_4 required if Ba^{2+} were present.

There is a drinking water softening plant in Cheam, England that uses the weak acid resin[5] for softening. After a cost analysis of alternative softening options including lime-soda softening, and after excluding any processes that released sodium into the drinking water, the authorities of Cheam decided to use the weak acid resin.

A weak acid resin Duolite C-433 manufactured by Diamond Shamrock was used for the University of Illinois study and Table 7 gives the characteristics of this resin.

TABLE 7. WEAK ACID RESIN CHARACTERISTICS

	C-433
Matrix	Polyacrylic
Crosslinking	Divinylbenzene
Functional Group	Carboxylic
Capacity	11.5 meq/g
Mesh Size	16 x 50
pH Range	5 - 14

Note that the capacity of the weak acid resin is 11.5 meq/g and much higher than the strong acid resin which had a capacity of 4.9 meq/g.

Steady State Condition (weak acid resin) --

Three sets of cyclic studies were performed to determine steady state characteristics that could be expected under full scale operation. A column with new resin was constructed and cyclic tests with the weak acid resin were performed. The column parameters and influent characteristics are given in table 8. Flow rates and other parameters are characteristic of full scale field conditions. Note that the alkalinity of 250 mg/L as $CaCO_3$ is greater than hardness of approximately 200 mg/L as $CaCO_3$ and, therefore, the weak acid resin would be capable of removing all of the divalent cations. Using the weak acid resin over the strong acid resin would be a good choice if alkalinity is greater than hardness.

TABLE 8. EXPERIMENTAL PARAMETERS FOR THE CYCLIC TESTS WITH WEAK ACID RESIN

	Test #1	Test #2	Test #3
Column length (cm)	60.6	60.6	60.6
Column diameter (cm)	2.5	2.5	2.5
Flow rate (gpm/ft^2; BV/hr)	4.3; 17.5	4.0; 16.4	4.1; 16.5
One bed volume (cm^3; g dry weight)	292; 110.7	292; 110.7	292; 110.7
Na^+ (mg/L)	24	51	25
Mg^{2+} (mg/L as $CaCO_3$)	92	98	100
Ca^{2+} (mg/L as $CaCO_3$)	97	102	98
Ba^{2+} (mg/L)	19	20	22
Total hardness (mg/L as $CaCO_3$)	195	200	198
Total alkalinity (mg/L as $CaCO_3$)	250	250	250
pH	6.8 - 7.0	6.8 - 7.0	6.8 - 7.0

The results of cyclic tests nos. 1, 2, and 3 are given in Tables 9, 11, and 12. The definitions for column utilization and regeneration efficiency were given in equations (1) and (2). Breakthrough capacity for the nine exhaustion cycles in Table 9 varied from 7.9 to 8.9 meq/g. In the first five cycles of cyclic test #1 (Table 9) regeneration efficiency varied from 76 to 88% when 10.4 meq HCl/g were used. These relatively low values of regeneration efficiency were caused by applying

TABLE 9. WEAK ACID EXHAUSTION-REGENERATION CYCLIC TEST #1

Cycle	Breakthrough Capacity (meq/g)	Column Utilization[a] %	Regeneration Efficiency[b,c] %	Terminal Hardness[d] (mg/L as $CaCO_3$)	Terminal Barium (mg/L)
1	8.9	77	79	41	0.2
2	8.4	73	76	60	0.2
3	8.4	73	81	42	0.1
4	8.8	77	88	68	0.1
5	8.0	70	79	54	0.4
6	7.9	69	88	44	0.1
7	8.2	71	91	47	0.3
8	8.0	70	91	42	0.2
9	8.3	72	95	47	0.2

a Maximum capacity: 11.5 meq/g
b Regenerant applied in cycles 1-5: 10.4 meq/g
c Regenerant applied in cycles 6-9: 9.0 meq/g
d Hardness is all magnesium

more regenerant than was necessary. After lowering the regenerant to 9.0 meq HCl/g of resin, the efficiency of regeneration increased to an average of 91% over the last four cycles. For all nine cycles, the terminal barium concentration did not exceed 0.1 to 0.4 mg/L. After the ninth exhaustion-regeneration cycle was completed, an additional 5.2 meq HCl/g of resin was applied (1.71 bed volumes of 3.58% (0.99N)) to remove any ions that remained on the resin. The total mass of magnesium, calcium, and barium removed during this final regeneration is listed in Table 10. After a cumulative total of 74.6 meq/g of metal ions were adsorbed over the nine cycles (avg = 8.3 meq/g/cycle), only 1.2% (0.097 meq/g) remained after the last cycle. This shows that with a regenerant dose of about 10% higher than the capacity utilized by divalent ions, the weak acid resin can be regenerated to essentially virgin capacity.

TABLE 10. IONS REMAINING ON THE WEAK ACID RESIN AFTER THE FINAL REGENERATION OF CYCLIC TEST #1

Mg^{2+} removed	0.06 meq/g
Ca^{2+} removed	0.03 meq/g
Ba^{2+} removed	0.007 meq/g

In cyclic tests #2 (table 11) a set of six exhaustion-regeneration cycles were performed using a regenerant dose of 7.6 meq HCl/g of resin. This regenerant dose was chosen to determine column performance when some of the metal ions were not removed from the column during regeneration. The breakthrough capacity decreased sharply between the first and second run. The column was incompletely regenerated after the first exhaustion run and thus the resin still contained some metal ions at the start of the second exhaustion run. This incomplete regeneration also resulted in a decrease in the percent column utilization (from 75% to 64%), an increase in regeneration efficiency to approximately 100%, and increased Ba^{2+} leakage at the start and end of the exhaustion run. The final barium concentration in the effluent at breakthrough after six column runs was 1.3 mg/L.

A seventh column run was also run as a part of cyclic test #2. Whereas, the first six column runs were completed at hardness breakthroughs between 40 and 77 mg/L $CaCO_3$ the seventh column run was carried out to 96 percent saturation with divalent metal ions. Results of exhaustion run seven are shown in Figure 4. Effluent profiles for calcium magnesium and barium are very similar to those found in column test with virgin resin (virgin resin breakthrough curves for weak acid resins are given in the full report, reference 1) with the exception that all of the ions appear in the effluent sooner. This was expected because a portion of the exchange capacity was not available due to

TABLE 11. WEAK ACID EXHAUSTION-REGENERATION CYCLIC TEST #2

Cycle	Breakthrough Capacity (meq/g)	Column Utilization[a] %	Regeneration Efficiency[b] %	Terminal Hardness (mg/L as $CaCO_3$)	Terminal Barium (mg/L)
1	8.7	75	105	51	0.5
2	7.8	68	103	47	0.8
3	7.8	68	101	77	1.9
4	7.6	66	101	70	1.6
5	7.4	64	101	50	1.3
6	7.4	64	102	40	1.3

a Maximum capacity: 11.5 meq/g
b Regenerant applied: 7.6 meq HCl/g

TABLE 12. WEAK ACID EXHAUSTION-REGENERATION CYCLIC TEST #3

Cycle	Breakthrough Capacity (meq/g)	Column Utilization[a] %	Regeneration Efficiency[b] %	Terminal Hardness (mg/L as $CaCO_3$)	Terminal Barium (mg/L)
1	8.0	70	95	45	0.2
2	7.8	68	96	42	0.0
3	7.8	68	95	46	0.1
4	7.8	68	96	42	0.1
5	7.8	68	93	38	0.1
6	8.2	71	94	43	0.2

a Maximum capacity: 11.5 meq/g
b Regenerant applied: 8.5 meq/g

incomplete regeneration. Figure 4 shows that there is hardness and barium leakage at the beginning of the column run. Hardness and barium in the effluent at the beginning of the column runs were a result of metal ions left on the column after the previous regeneration. Metal ions that are not removed during regeneration will be concentrated at

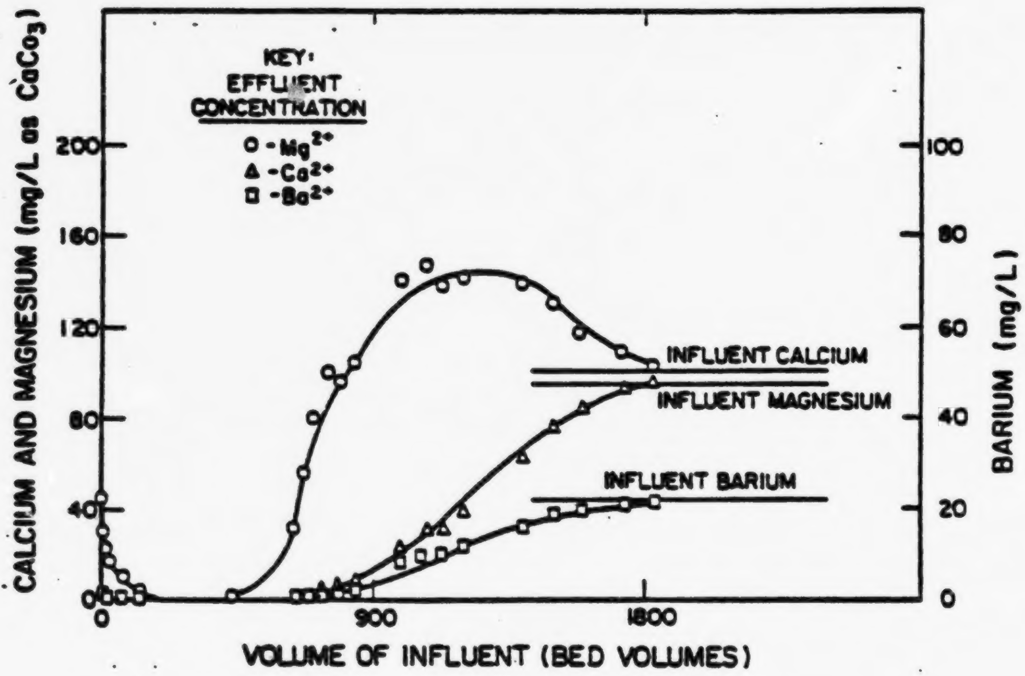

Figure 4. Weak acid resin breakthrough curves for run #7 of cyclic run #2. Regenerant dose was 7.6 meq HCl/g.

the effluent end of the resin column and these ions will come off the resin at the beginning of the next cycle.

Cyclic test #3 (Table 12) consisted of six exhaustion-regeneration cycles that were performed with a regenerant dose of 8.5 meq HCl/g of resin. This regenerant level was chosen to examine the column performance at a level of regenerant intermediate to the previous two doses. The results are listed in Table 12. Breakthrough ranged from 7.8 to 8.2 meq/g and column utilization ranged from 68 percent to 71 prcent. There was no sharp decrease in breakthrough capacity over the first two runs as in cyclic test #2. This indicates that most of the metal ions were removed during regeneration and near virgin capacity was retained from cycle to cycle.

Regeneration efficiency averaged 95% for the six-column run, which was slightly lower than that experienced in cyclic test #2, in keeping with the application of a greater amount of regenerant than metal ions removed. The waste brine volume was 1.2 BV/100 BV of product water with a TDS of 19,900 mg/L.

The effluent barium concentrations ranged from 0 to 0.2 mg/L for breakthrough hardness concentrations of 46 mg/L as $CaCO_3$ or less. Barium concentrations in this range are at the lower end of the detection limits of ion chromatography, and therefore it was difficult to measure exact concentrations. However, it is safe to conclude that barium removal was more than acceptable for this set of runs.

Hardness and barium concentration profiles are shown in Figure 5 for the sixth exhaustion run of cyclic test #3. There was only minor hardness and barium leakage at both the beginning and end of the run;

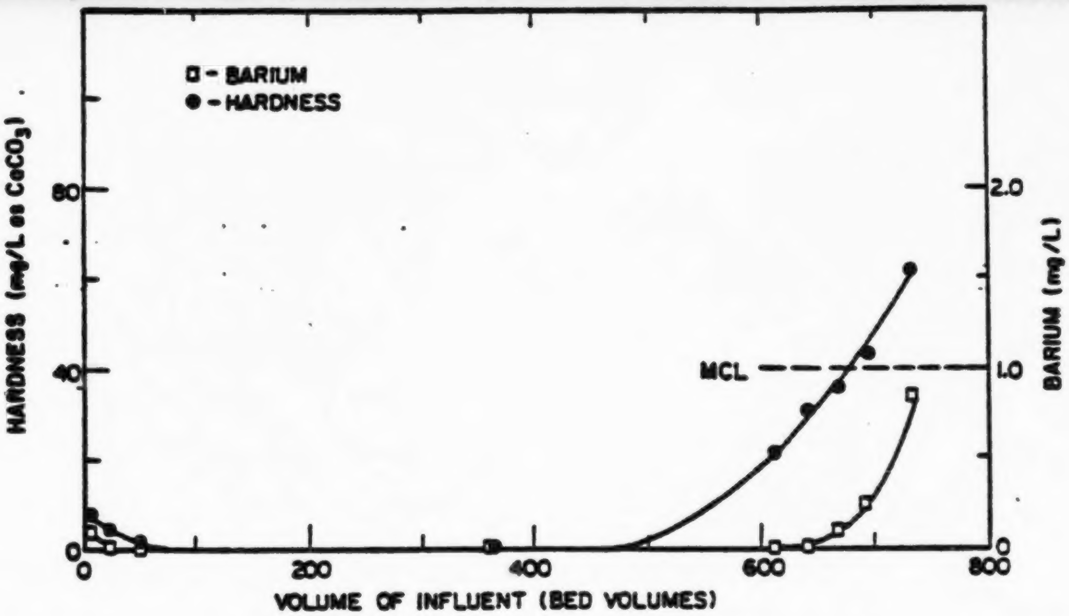

Figure 5. Weak acid resin breakthrough curves for run #6 of cyclic run #3. Regenerant dose was 8.5 meq HCl/g.

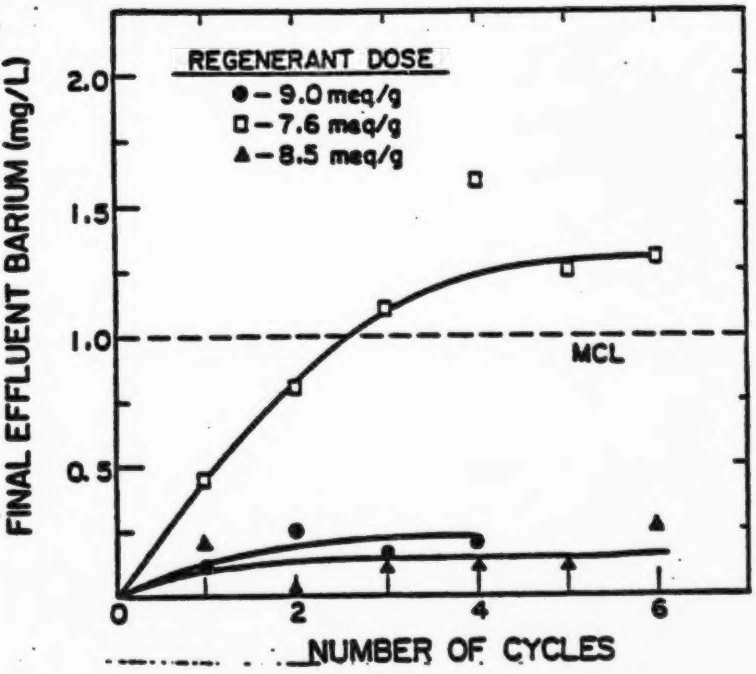

Figure 6. Barium concentration at the termination of weak acid resin cyclic tests.

thus it appears that a still lower regenerant dose, perhaps 8.0 meq HCl/g, would give satisfactory performance.

Regenerant dose --

The barium removal performance of each of the cyclic tests is summarized in Figure 6. The final barium concentrations are plotted for the last four runs of cyclic test #1 and for the first six runs each of cyclic tests #2 and #3.

For regenerant doses of 8.5 and 9.0 meq HCl/g, the barium concentration levels off considerably below the MCL of 1.0 mg/L. On the other hand, when a regenerant dose of 7.6 meq HCl/g was applied as in cyclic test #2, concentrations of barium were found to be greater than 1.0 mg/L. The optimum dose for the water treated in these experiments lies between 7.6 and 8.5 meq/g, and quite likely is about 8 meq/g. This value will also be a function of the quality of water treated and probably will vary with the ratios of barium to hardness, hardness to alkalinity, and hardness to other divalent metal ions. Further research is needed to establish these functions.

Radium Removal (weak acid resin) --

The results of a column run using virgin weak acid resin for Ra-226 removal are given in table 13. The influent radium concentration averaged 18.6 pCi/L while the influent hardness concentration averaged 193 mg/L as $CaCO_3$. Effluent radium concentrations (Table 13) are below the MCL of 5 pCi/L. As with the strong acid resin, there was no significant increase in Ra-226 concentration long after hardness breakthrough.

Since radium-226 removal occurred even after the resin was saturated with hardness during virgin resin column tests (Table 13), it appears that the weak acid resin has a very high selectivity for radium.

TABLE 13. RADIUM REMOVAL, WEAK ACID VIRGIN RESIN COLUMN TEST
(average influent radium concentration = 18.6 pCi/L)

Bed Volumes of Influent	Effluent Hardness (mg/L as $CaCO_3$)	Effluent Radium (pCi/L)
25.6	<1.0	2.5
426.2	<1.0	2.8
671.9	<1.0	3.1
915.5	108	3.0
986.6	148	3.2
1167.1	198	3.0

NOTE: These samples were analyzed in the Environmental Research Laboratory, University of Illinois, Urbana, IL.

To determine whether the Ra-226 was held so tightly that it could not be removed during regeneration, the mass of Ra-226 removed during regeneration was determined and compared to the amount that was applied (see table 14). The mass of radium applied was determined from the influent concentration and the volume of influent applied, while the mass of radium removed was measured by the volume of spent regenerant brine and rinse and its concentration. The amount that passed through the column during the exhaustion cycle was assumed to be negligible. Table 14 shows that the mass removed is approximately equal to the mass applied so there is no indication of significant accumulation of radium on the weak acid resin.

TABLE 14. RADIUM MASS APPLIED vs. MASS REMOVED DURING REGENERATION OF WEAK ACID RESINS

Cyclic Test	Cycle	Mass Applied (pCi)	Mass Removed During Regeneration (pCi)	% Applied that was Removed
2	4	3735	-	
	6	3125	3830	123
3	5	3456	3479	101
	6	3627	3181	88

NOTE: Samples were analyzed by the Environmental Research Laboratory, University of Illinois and the University Hygienic Laboratory, University of Iowa.

The performance of the weak acid resin for radium-226 removal was also measured during the three cyclic column tests (Tables 9, 11 and 12). Influent and effluent samples were analyzed for a number of the runs in each of the three tests; the effluent samples were composites of the entire exhaustion cycle. The results are given in Table 15. Radium removal percentages were comparable for all three cyclic tests, and varied between 90-98%. Regenerant dose varied from 7.6 to 9.0 meq HCl/g and seemed to have little effect on radium removal. Effluent radium concentrations varied from 0.4-2.0 pCi/L, which are well below the MCL of 5 pCi/L. These results are similar to those for the strong acid resin.

TABLE 15. RADIUM REMOVAL, WEAK ACID RESIN CYCLIC TESTS

Cyclic Test #	Run #	Influent	Effluent	% Removed
1	3	19.3*	2.0*	90
	4	16.1*	0.8*	95
2	4	18.5	0.7	96
	6	16.0		
3	1	19.1	0.4	98
	2	20.0	0.6	97

*130 mL samples were analyzed for these samples, all others were 1000 mL.

NOTE: Samples were analyzed by the Environmental Research Laboratory, University of Illinois, Urbana, IL.

Calcium Cation Exchange

Complete removal of hardness from water is often not appropriate or desirable. Low-calcium waters are corrosive to some extent and removing this low quantity of hardness in order to remove barium and/or radium may be undesirable. The strong-acid resin has a higher selectivity for barium and radium than calcium and magnesium and thus a resin in the calcium-form will selectively remove barium and radium from water.[6] Tests for barium removal were run on calcium-form resin using water with the influent composition given in Table 16. The number of bed volumes that can be processed depends on the quantity of calcium chloride regenerant applied as shown in Figure 7. Application of 4, 6, and 8 equivalents of calcium/L of resin resulted in runs of 500, 900, and 1000 bed volumes respectively, compared with 1,200 bed volumes for virgin resin when influent barium concentration was 23 mg/L. The trade off between resin capacity per run and regeneration efficiency is shown in Figure 8.

TABLE 16. COMPOSITION OF INFLUENT WATER

Parameter	Concentration
Total hardness	215 mg as $CaCO_3$/L
Calcium	105 mg as $CaCO_3$/L
Magnesium	95 mg as $CaCO_3$/L
Barium	23 mg/L
Sodium	23 mg/L
Chloride	10 mg/L
Total Alkalinity	250 mg as $CaCO_3$/L
pH	7

The ability of a calcium-form resin column to remove radium from water was evaluated through four exhaustion-regeneration cycles. The fifth cycle consisted of exhaustion only. Influent water was similar to that shown in Table 16, except that 43 pCi radium/L replaced the barium. Exhaustion in 4.7-in (12 cm) column was carried out at 1.35 gpm/ft^2 (3.4 m/hr) for 500 bed volumes. Termination of the run at 500 bed volumes was arbitrary; additional runs are needed to establish the number of bed volumes that can be processed to radium breakthrough. Regenerant brine contained 34,000 mg/L calcium and 4,860 mg/L magnesium. The brine-loading rate ws 0.29 gpm/ft^2 (0.7 m/hr), and the dose was 6 equivalents of calcium/L resin (27.51b $CaCl_2 \cdot 2H_2O/ft^3$ resin). The spent brine from each cycle was reclaimed and reused in the next cycle. Rinse-water volume was 8.5 bed volumes.

The average radium concentration in the effluent in each of the five exhaustion runs was <0.5 pCi/L (98.8 percent radium removal). The amount of radium placed on the column during exhaustion was 45 pCi/g dry resin (0.02 uCi/L resin). Radium capacity at breakthrough was not determined.

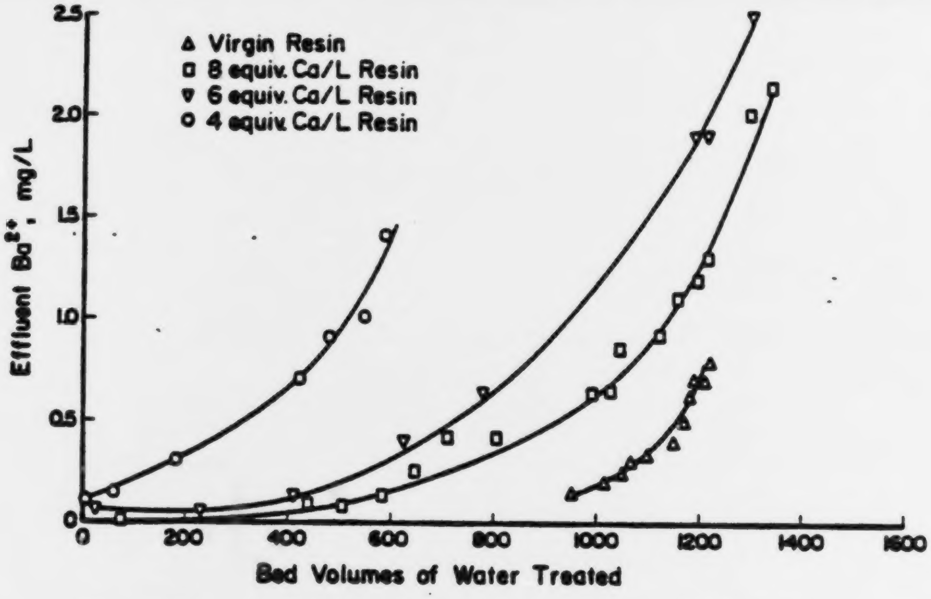

Figure 7. Barium breakthrough curves at different regenerant dosages.

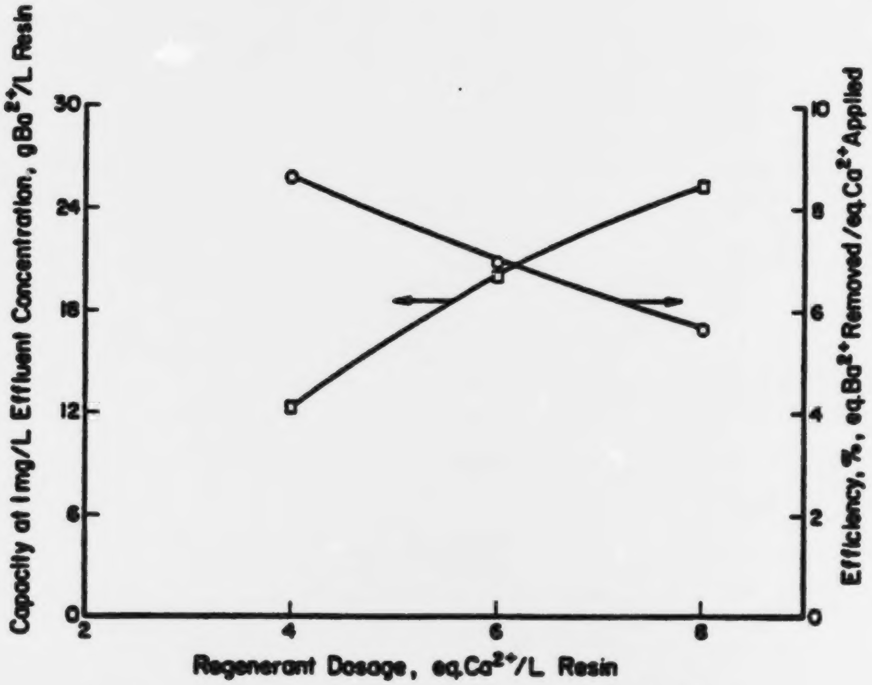

Figure 8. Regeneration efficiency and column capacity at various regenerant dosages.

The spent $CaCl_2$ brine can be reclaimed for reuse. Addition of 10 percent molar excess solid $CaSO_4$ (relative to the barium in the brine) resulted in reduction of the barium concentration to about 100 mg/L. The $CaSO_4$ dissolved, and $BaSO_4$ precipitated. Use of a very soluble sulfate salt such as sodium sulfate was not successful because high localized concentrations of sulfate caused $CaSO_4$ as well as $BaSO_4$ to precipitate. Reuse of brine was possible after removal of the precipitate by filtration. The concentration of magnesium in the brine increased through successive cycles until a plateau value was reached. This resulted in a column that was partially in the magnesium form at the beginning of an exhaustion run. This does not pose a problem because barium and radium can replace magnesium more easily than calcium. If the brine contains radium as well as barium, the radium will also be removed by coprecipitation with the $BaSO_4$. However, a barium salt such as $BaCL_2$ will have to be added along with the $CaSO_4$ to the spent $CaCl_2$ brine containing only radium to achieve radium removal.

Additional research is needed to refine the brine reclamation process. In particular, the base procedure to precipitate and separate barium and radium needs to be established. A procedure is also needed to control the precipitation process to ensure that the barium and radium have been removed and that too much sulfate has not been added. The brine reclamation process should significantly reduce the brine disposal problem, but ways of disposing of the precipitate must be found, and the cost involved in using the process must be established.

Strong acid resins remove practically all of the hardness from the water. Complete hardness removal is not necessary or desirable and therefore blending of treated and untreated water is usually practiced to prevent pipeline corrosion and reduce costs. Waters with less than 50 mg/L as $CaCO_3$ hardness are considered soft and waters with up to 150 mg/L as $CaCO_3$ hardness are considered moderately hard. Blending is usually practiced to obtain a finished water hardness of about 100 mg/L as $CaCO_3$. If blending increases the radium concentration above the MCL, then calcium cation exchange should be used to remove radium from the by-pass water.

SECTION 5

IRON AND MANGANESE REMOVAL
(University of Iowa Study)[7]

SUMMARY OF IRON AND MANGANESE REMOVAL

Previous field studies[8,9,10] have shown that anywhere from 10 to 53% radium removal takes place across iron removal processes that consist of aeration, detention, and filtration. The primary objective of the University of Iowa Study was to determine the variables that control this incidental removal of radium and to evaluate the possibility of expoliting these factors to provide an inexpensive means of removing radium using existing or modified iron removal facilities. This study investigated how water chemistry influences Ra-226 sorption to iron and manganese oxides and sorption to filter sand.

The potential for significant radium sorption to hydrous iron oxides under typical ground water conditions is limited by too low an iron concentration in the presence of barium, calcium, and magnesium which are believed to compete for sorption sites. Sorption to iron oxides increased with pH but significant sorption to iron oxides at iron concentrations typical of natural waters would require excessive pH values. Batch studies using freshly precipitated iron oxides, formed in the laboratory, showed that sorption of radium from typical groundwaters is generally expected to result in maximum removals of approximately 10 to 20% and should be much less.

Radium removals obtained by freshly precipitated hydrous manganese oxides in batch studies were much greater than those obtained in systems containing only iron oxides. Radium removals by manganese oxides were significantly greater in hardness free waters because of less competition by hardness ions. In the absence of iron, 1.0 mg/L MnO_2 removed approximately 65% of the Ra-226 from Oxford, Iowa water (hardness = 1300 mg/L as $CaCO_3$) at pH 7.5. Sorption to MnO_2 appears to be a good radium removal mechanism if sorption of ferrous ion and coating of the manganese oxides with iron oxides can be eliminated.

Filter sand has a potential capacity to sorb significant concentration of radium at typical hardness concentrations if the capacity is maintained by periodically rinsing the sand with a dilute acid. Removal efficiencies of approximately 80-90% were achieved in laboratory and field studies using a 61 cm (2 ft) deep sand bed at conventional loading rates when daily rinsing with a dilute acid was practiced. Radium sorption to filter sand increases with pH but is not very sensitive to pH in the range of pH 5 to 8 or to hardness concentrations above approximately 300 mg/L as $CaCO_3$.

The following is a more detailed discussion of the University of Iowa Study.

TESTING PROCEDURES

Batch studies, laboratory pilot plant studies and field pilot plant studies at Oxford, Iowa were performed.

Batch studies as shown in Figure 9 were conducted at 25°C using 2 liter beakers stirred with a Birds and Phipps gang stirrer. Mixtures of varying carbon dioxide and air were bubbled through to provide pH control although pH was also adjusted in several experiments by adding concentrated sulfuric acid or sodium hydroxide. Solutions containing pure iron oxides were generally prepared by first deaerating the water by purging with nitrogen gas, adjusting pH to approximately 6.5 by bubbling pure carbon dioxide, and then adding ferrous sulfate and

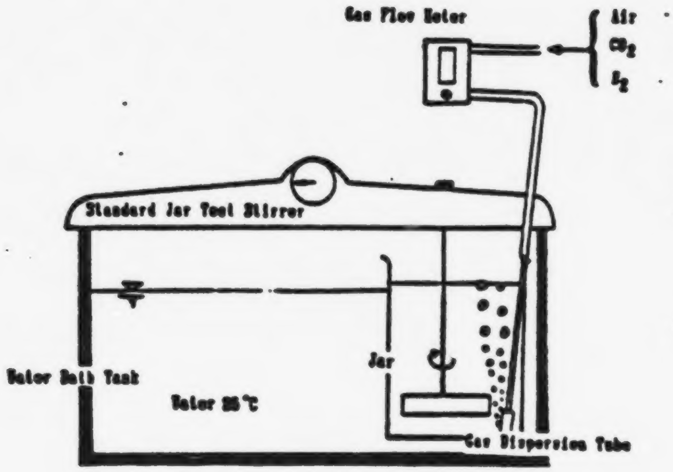
Gas Flow Meter
Air
CO_2
N_2
Standard Jar Test Stirrer
Jar
Water Bath Tank
Water 25°C
Gas Dispersion Tube

Figure 9. Schematic diagram of batch jar test apparatus

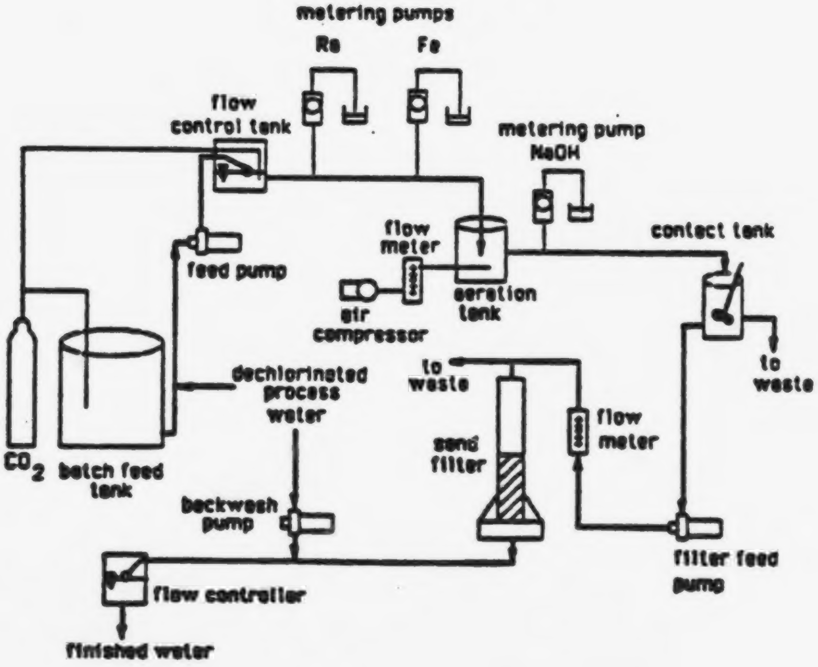
metering pumps
Ra
Fe
flow control tank
metering pump NaOH
flow meter
contact tank
feed pump
air compressor
aeration tank
to waste
dechlorinated process water
to waste
flow meter
sand filter
CO_2
batch feed tank
backwash pump
filter feed pump
flow controller
finished water

Figure 10. Schematic diagram of pilot plant

Ra-226. The solutions were then aerated to approximately pH 8 with air to oxidize the iron. The pH was then adjusted to the desired value by bubbling buffer gas (or acid/base addition) followed by aging for one hour. Solutions of pure manganese oxides were prepared similarly by using stiochiometric amounts of permanganate to oxidize added manganous ion. Sorption onto acid washed and dionized water rinsed 0.5 mm filter sand (effective size) was studied using the same apparatus.

Laboratory pilot plant studies were conducted using the iron aeration-sand filtration pilot plant shown in Figure 10.

The 10.2 cm (4 in) diameter pressure sand filter was filled with 61 cm (2 ft) depth of filter sand and equipped for water backwashing and periodic rinsing with dilute acid. Ra-226 and ferrous iron could be added to the water which was maintained at pH 6.5 prior to aeration by bubbling caron dioxide through it. Aeration to approximately pH 7.5 was accomplished in a tank having a 10 minute hydraulic residence time. Filter influent was withdrawn from a small tank used to moderate flow. Flow rate through the filter was controlled using a small constant head tank equipped with a flow control float and valve. Automatic samplers were used to obtain discrete and composite samples. The water supply was usually 18°C + 3°C.

Field studies at Oxford, Iowa utilized a similar pressure filter equipped for rinsing with a dilute acid in addition to water backwashing. Water temperature was usually 15°C ± 3°C.

TYPES OF WATERS USED

Batch studies were conducted using synthetic groundwaters and groundwaters obtained from Oxford, Iowa and Eldon, Iowa. A hardness free synthetic water (referred to as Na-form water) was prepared by mixing 5 mM $NaHCO_3$, 1 mM Na_2SO_4 and 1 mM NaCl to deionized water. Calcium and/or magnesium sulfate was added to vary hardness. Finished waters were obtained from Oxford and Eldon, Iowa and were filtered through a 0.45 micron filter prior to use. Oxford water had a hardness and alkalinity of approximately 1300 mg/L and 300 mg/L as $CaCO_3$ respectively. Eldon water had a total hardness and alkalinity of approximately 300 mg/L and 200 mg/L as $CaCO_3$ respectively. Oxford and Eldon water contained approximately 10 pCi/L and 50 pCi/L of natural Ra-226 respectively. Radium concentrations were increased by adding additonal Ra-226. Laboratory pilot plant studies were conducted using the tap water obtained at the University of Iowa Hygienic Laboratory which had a total hardness of approximately 150 mg/L as $CaCO_3$ and an alkalinity of approximately 300 mg/L as $CaCO_3$. Field studies at Oxford utilized the existing sand filter effluent (iron floc removed) or aeration tank effluent (containing iron floc).

RESULTS AND DISCUSSION

Sorption to Hydrous Iron Oxides

Effect of pH --

Figure 11 shows the effect of pH on Ra-226 removal in the presence of 10 mg/L iron oxides in Na-form water (no Ca or Mg present). The importance of pH control is clearly demonstrated by an increase in removal from 30 to 40% near pH 7 to approximately 80% near pH 8. The shape of the curve shows that radium removal by sorption to iron oxides is very sensitive in the pH range of 7 to 8 which is typically encountered in water supplies. This may explain some of the differences that took place in earlier sampling between treatment plants.[8]

Removal Mechanism --

Figure 12 shows that surface sorption of radium onto the iron oxide surface takes place and not incorporation of radium into the ferrous ion as oxidation is taking place. In Figure 12 slow precipitation (Slow - pptn), radium was added initially in the presence of ferrous ion before aeration and then radium was added after the iron was oxidized, post-precipitation (Post-pptn) and approximately 70 to 75% radium was removed in both cases. This clearly shows that the mechansism of removal is surface sorption onto the iron oxide surface. In Figure 12 (Fast-pptn), ferrous iron was added to an aerated solution containing radium which resulted in nearly instantaneous formation of iron oxides. This shows that the rate of iron oxide formation did not affect the amount of radium adsorbed. Similar trends are shown over a wide pH range in Figure 13 which shows no difference between fast and slow precipitation. These results show that differences in oxidation rates encountered in the field would not explain observed differences in radium adsorption. Sorption of radium to iron oxides appears to be very rapid but changes in iron oxide surface characteristics, such as coating with hardness or ferrous ion, could occur with time which would affect adsorption.

Effect of Iron and Radium Concentration on Sorption --

The relationship between sorbent (hydrous iron oxide concentration) and sorbate (R-226 concentration) was characterized by a linear sorption isotherm. The sorption isotherm can be used here to estimate the capacity of iron oxides for radium and the equilibrium concentrations of radium that remain. Isotherms are typically developed in experiments by varying either and/or both sorbent and sorbate. Figure 14 developed form sodium from water corresponds to a linear isotherm

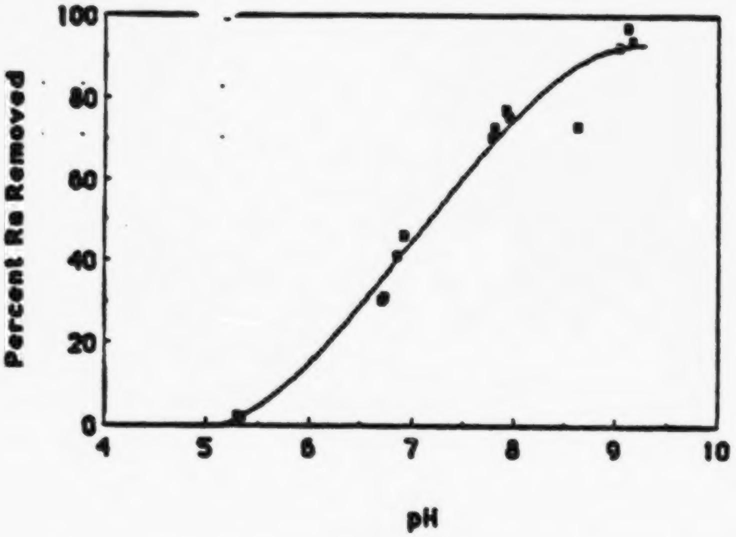

Figure 11. The effect of pH on radium removal in the presence of iron oxides

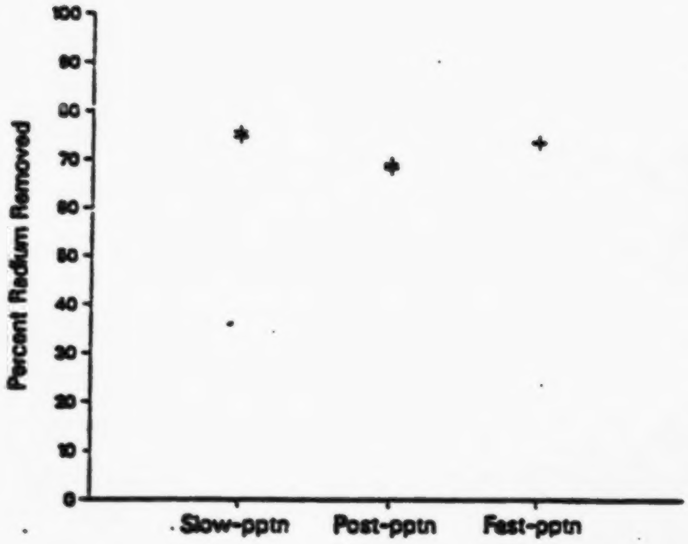

Figure 12. Percent radium removed by iron oxides: Comparison of precipitation methods at pH 7.8 in Na-Form synthetic water. Fe = 10 mg/L (as Fe), Ra = 48 pCi/L.

that gives the amount of radium remaining in solution on the abscissa and the amount of radium sorbed per unit mass of iron present on the ordinate. Considerable scatter is apparent, but sorption appears to reasonably follow a linear isotherm. The following equation describes the linear isotherm given in Figure 14:

$$q = K_d\ [\text{Ra-226}] \qquad (7)$$

where

q = amount of radium sorbed per unit mass of iron

K_d = distribution coefficeint

$K_d = 0.23 \dfrac{\text{pCi/mg Fe}}{\text{pCi Ra-226/L}}$ for Fig. 14

Ra-226 = concentration of radium remanining in solution

If a linear isotherm is assumed, then percent radium sorbed is related to total iron concentration by the following equation:

$$\%\ \text{Ra sorbed} = 100\ K_d\text{Fe}/[1 + K_d\text{Fe}] \qquad (8)$$

where

K_d = distribution coefficient

Fe = total iron concentration

Figure 15 is a graph of equation 8 showing the concentration of iron in oxidized form that is required to remove radium under ideal conditions (no other divalent cations present).

Iron concentration in water supplies is usually less than 5 mg/L and therefore Figure 15 shows that you would expect less than 53% radium removal in water that has no hardness. Hardness concentration is usually high in well water and radium concentration would be in the order of 10^{-12} g/L, therefore, since hardness exists in much higher concentations and is competing with radium for sorption sites, very little little sorption of radium onto iron floc would be expected.

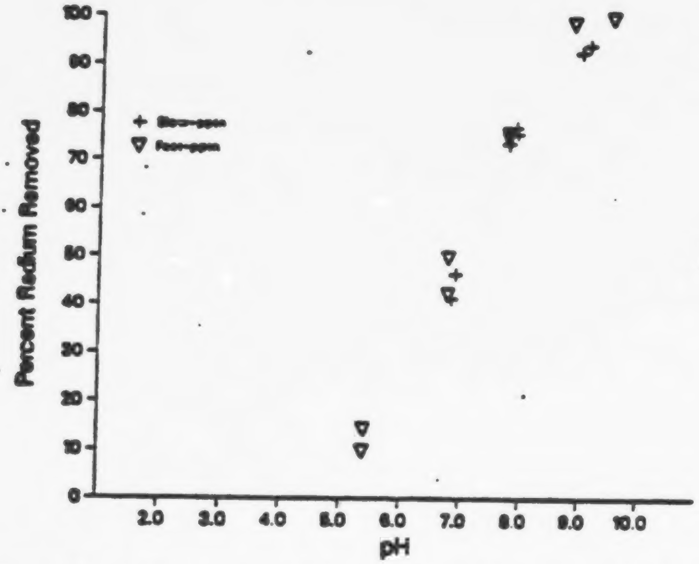

Figure 13. Percent radium removed by iron oxides as a function of pH: Comparison of the "fast" vs "slow" method of iron oxide formation in Na-Form Synthetic Water. Fe = 10 mg/L (as Fe), Ra = 48 pCi/L.

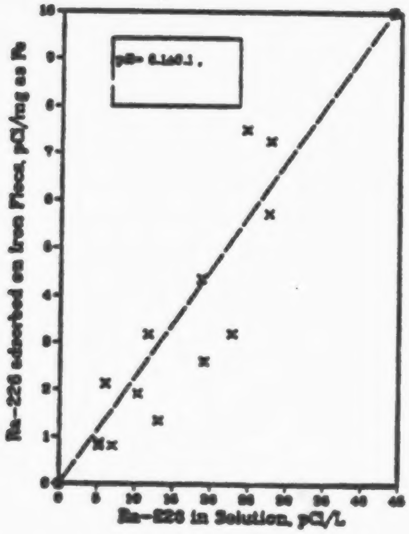

Figure 14. Radium adsorbed on iron vs radium concentration remaining in solution

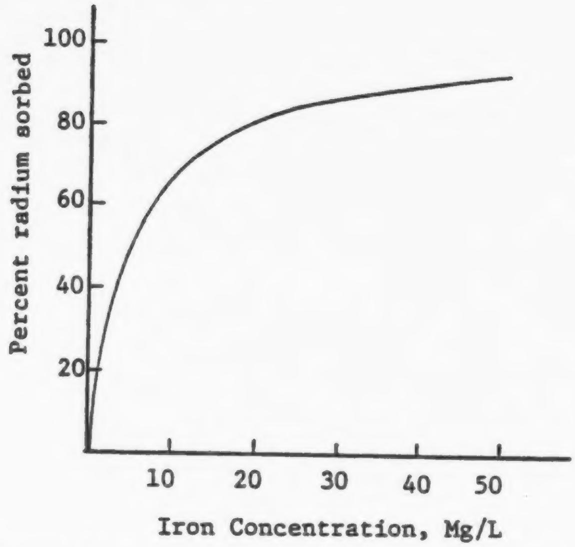

Figure 15. Percent radium sorbed as a function of iron concentration when no other divalent cations are present

Effect of Competing Ions --

The amount of radium sorbed onto iron flocs decreases as the concentration of divalent ions such as barium, calcium and magnesium increases. Relatively small amounts of barium greatly decrease radium sorption, as shown in Table 17, obtained in Na-form water at pH 8.1. A minimum radium removal of approximately 31% was obtained at approximately 0.5 mg/L barium as compared to about 74% removal obtained in its absence. Increased removals observed at barium concentrations in excess of 1 mg/L (Table 17) are believed attributable to co-precipitation with $BaSO_4$ which probably formed. This likelihood is indicated by the increasing proportion of barium removed from solution as the barium is increased above 1 mg/L. Radium sorption to iron oxides is expected to be adversely affected by barium in natural waters unless the barium is significantly complexed and not available for competitive sorption.

TABLE 17. THE RELATIONSHIP OF BARIUM ION CONCENTRATION TO RADIUM REMOVAL BY IRON OXIDES†

Dosed Barium mg/L	Soluble Barium mg/L	Removed Barium* mg/L	Radium Removal percent
0.	-		74
0.01	<0.05		58
0.1	0.075	0.025	49
0.5	0.315	0.185	31
1.0	0.598	0.402	32
2.0	0.250	1.750	59
5.0	0.340	4.660	72

†All the values are averages, Na-form water, pH = 8.1
*Removed barium = Dosed - Soluble

The effect of calcium and magnesium on sorption to iron oxides is shown in Figures 16 and 17 which show examples of Oxford, Iowa and Eldon, Iowa waters with hardness of 1300 mg/L and 300 mg/L as $CaCO_3$, respectively. Radium sorption by 10 mg/L of iron oxides formed by the slow-pptn method in Oxford and Eldon, Iowa, was significantly less above pH 7 than obtained when Na-form synthetic groundwater was used as shown in Figures 16 and 17. In these experiments naturally occurring radium was augmented to 49 and 78 pCi/L for Oxford and Eldon, Iowa, water, respecitvely. Percent radium removed was similar for both natural waters and was approximately 10 and 15% at pH 7.0 in the Eldon and Oxford waters, respectively, and about 20% at pH 8 for both waters. This similarity is in spite of the great differences in total hardness (1300 mg/L vs. 300 mg/L as $CaCO_3$ for Oxford vs. Eldon water) but is expected based on the observation that above approximately 300 mg/L Ca as $CaCO_3$, calcium does not cause a further significant reduction in sorption. The somewhat better removal in Oxford water obtained at pH 7 is not believed to be significant in comparison to that obtained in the Eldon water. Radium removals at iron concentrations less than 10 mg/L are expected to be lower.

Comparison of Sorption to Natural and Synthetic Iron Oxides --

A series of experiments were conducted to compare radium sorption to natural iron oxides with that onto synthetic iron oxides typical of those used in this study. Natural iron oxides were obtained from the backwash of the existing filter at the City of Oxford and were washed in distilled water six times prior to experimental use. Experiments using natural oxides were conducted at a total radium concentration of 32 pCi/L which required augmentation of existing radium in the Oxford water.

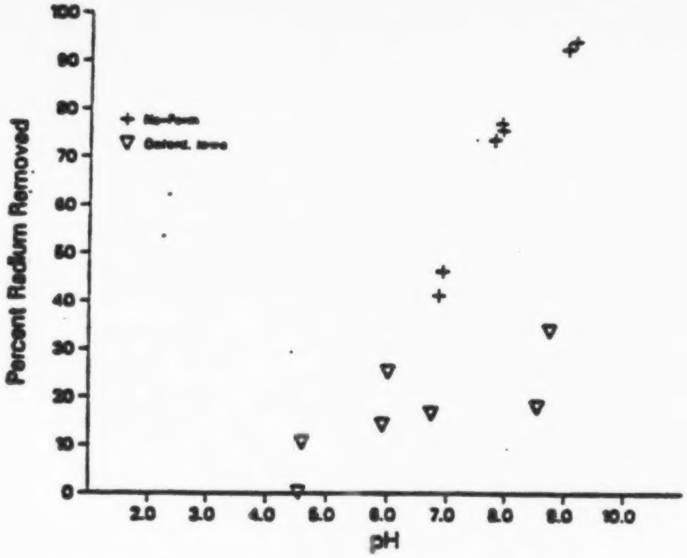

Figure 16. Percent radium removed by iron oxides as a function of pH: Na-Form synthetic water (48 pCi Ra/L) vs Oxford groundwater [8.5 mM Ca, 4.1 mM Mg, 49 (7.5 natural) pCi Ra/L] Fe = 10 mg/L (as Fe)

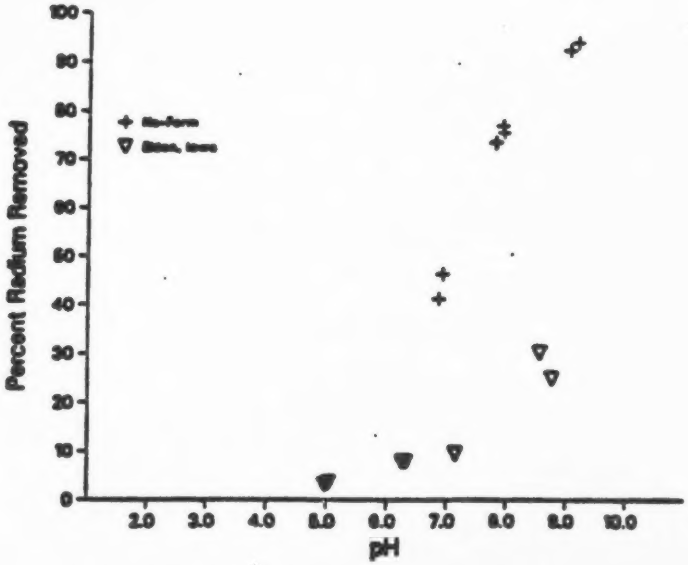

Figure 17. Percent radium removed by iron oxides as a function of pH: Na-Form synthetic water (48 pCi Ra/L) vs Eldon groundwater [2 mM Ca, 1 mM Mg, 78 (50.8 natural) pCi Ra/L] Fe = 10 mg/L (as Fe)

Figure 18 shows the pH dependence of sorption of radium onto natural iron oxides in both the hardness free synethetic groundwater and in Oxford water. Much higher removals were obtained in the synthetic water as compared to those obtained in Oxford water. This is similar to results obtained using synthetic iron oxides.

Removals obtained using natural iron oxides cannot be directly compared with removals obtained using 10 mg/L Fe of synthetic iron oxides because the experiments using natural oxides utilized 7.5 to 8.2 mg/L Fe. However, all natural oxide experiments can be normalized to results expected at 10 mg/L through the use of calculated partition coefficients (K_d values). Figure 19 is a comparison of percent radium removal for the natural oxides at 10 mg/L Fe concentrations with removals obtained using 10 mg/L synthetic oxides. Normalized results for both types of iron oxides in synthetic groundwater and Oxford water are very similar. Therefore it would appear that results obtained using the experimental synthetic system can be extrapolated to actual field conditions. Again the reader is cautioned not to over generalize this conclusion as it does not prove that synthetic and natural oxides will in general yield similar results. In fact, these results are quite unexpected.

Sorption onto Manganese Oxides

Pure Manganese Oxides --

Ra-226 sorption to 1 and 5 mg/L manganese oxides (as MnO_2) produced by oxidation of manganous ion from the stoichiometric addition of potassium permanganate in Na-form water was significant over the pH range of approximately 5.5 to 9.2 (Figure 20). Average removals were about 80 - 90% for both concentrations above a pH of about 6.5 and were

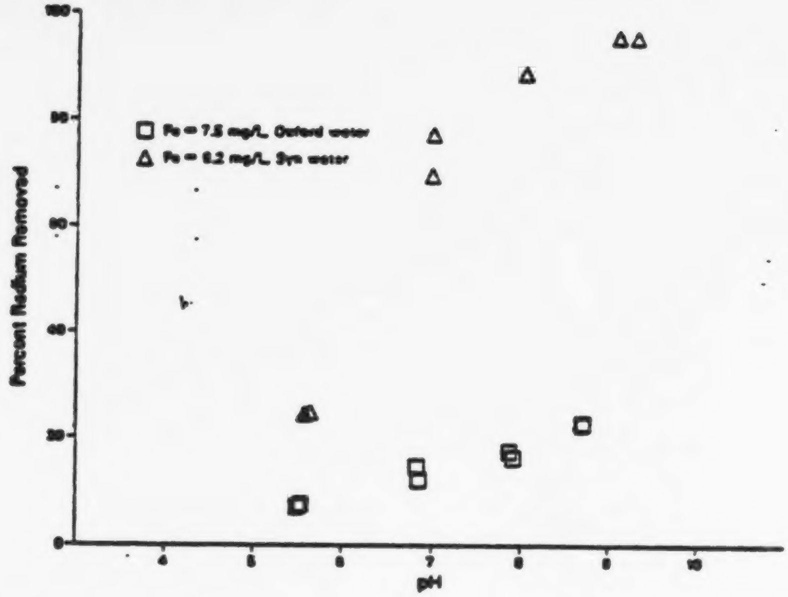

Figure 18. Percentage of radium removed by iron oxides in Na-synthetic and Oxford groundwater

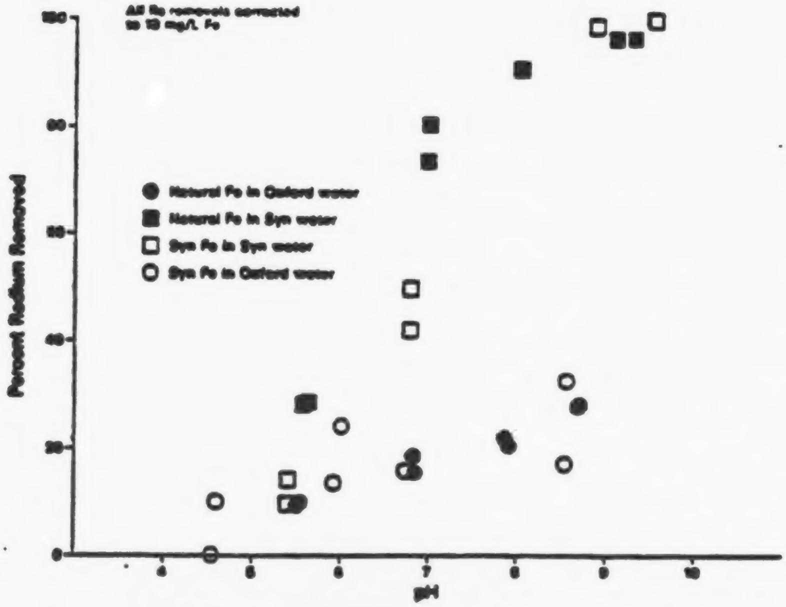

Figure 19. Percent radium removed by natural and synthetic iron oxides in synthetic and Oxford water. Results normalized to 10 mg/L Fe.

not significantly decreased by the presence of 1 and 3 mM calcium (100 and 300 mg/L as $CaCO_3$). These removals are much greater than determined for the pure iron oxide system at comparable molar concentrations and were not as sensitive to calcium and pH. The higher sorptive capacity is expected based on the lower point of zero charge (pzc) for manganese oxides.

Radium removals in Oxford water were much greater in the pure manganese oxide system as shown in Figure 21 when compared to comparable iron oxide systems. Significant removals of 60 - 80% were observed over the pH range of approximately 6.6 to 9 in the presence of 1 mg/L MnO_2 (same molar concentration obtained by oxidation of 1.57 mg/L Fe). Removals exceeded 80% in the presence of 5 and 10 mg/L MnO_2 at comparable pH values. Dilution with 50% distilled water also did not cause a significant increase in removal in spite of the reduction in hardness from approximately 1300 to 650 mg/L as $CaCO_3$.

Mixed Iron/Manganese Oxides --

A possible radium treatment strategy would involve the use of potassium permanganate to oxidize iron (or manganese). In the presence of iron, mixtures of iron and manganese oxides would form. The presence of ferrous ion could inhibit radium sorption to manganese oxides, because of competition with radium for sorption sites. Sorption to mixed iron/manganese oxides was studied in several experiments by the addition of enough potassium permanganate to cause an oxidation of 90% of the available ferrous iron. 1 mg/L of Fe^{2+} would produce 0.42 mg/L of MnO_2 as MnO_2 from $KMnO_4$ addition.

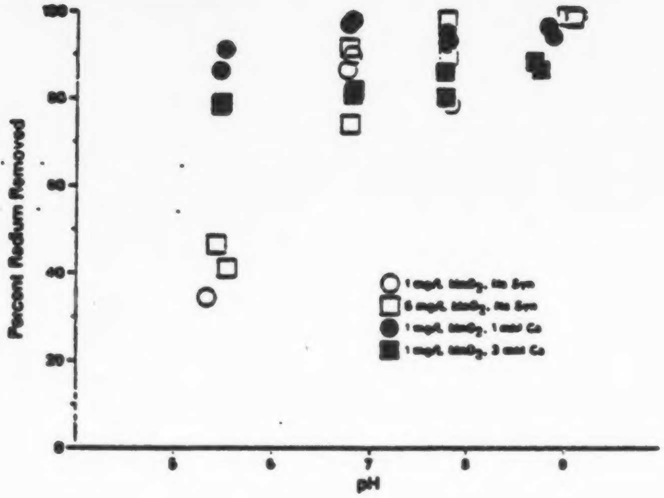

Figure 20. Radium removal in Na-Form synthetic water by 1 and 5 mg/L MnO_2 (as MnO_2). Ra = 32 pCi/L.

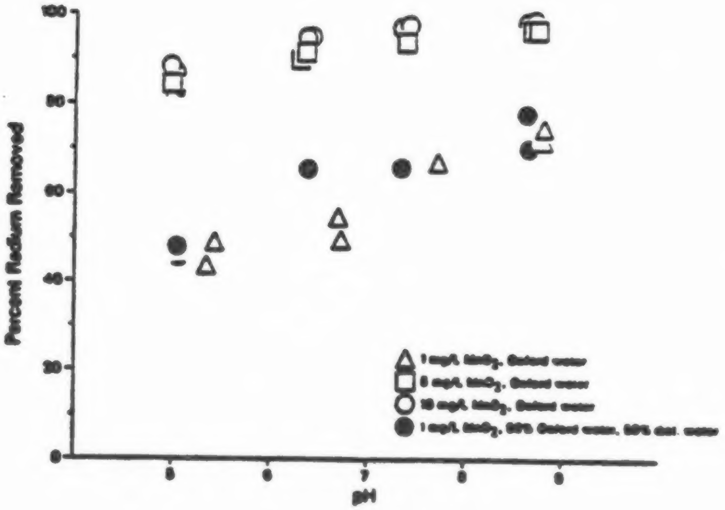

Figure 21. Radium removal by MnO_2 in Oxford water. Ra = 32 pCi/L

Sorption of Ra-226 from Na-form water was much greater in the mixed oxide systems than in the presence of comparable concentrations of iron alone (Figure 22). For example, radium removal by 1 mg/L Fe plus 0.4 mg/L MnO_2 was generally much greater than that obtained in the presence of 10 mg/L Fe alone. Sorption by the mixed oxides in Oxford water was significantly less (Figure 23), than obtained in the Na-form water. Removals of approximately 10% were obtained in the 2.0 mg/L Fe-0.8 mg/L MnO_2 system in Oxford water. This can be compared with results in Figure 21 showing that 1 mg/L of pure MnO_2 brought about a 60 - 80% reduction of radium in Oxford water. Similar conclusions can be made regarding removals from Oxford water in the 5 mg/L and 2.0 mg/L Fe-MnO_2 system. Therefore, it appears that iron does interfere to some extent with sorption to manganese oxides if all other factors are the same.

Sorption to Filter Sand

During the course of the University of Iowa study the investigator discovered considerable sorption of radium to filter sand. The investigator pursued this phenomena in an effort to see if existing sand filters at iron removal plants could be optimized to remove radium to a concentration below the MCL.

Effect of pH in Absence of Hardness --

Sorption generally increased with pH as shown in Figure 24 for data obtained using 10 g/L sand and no hardness. Figure 24 shows that radium sorption was a weak function of pH above pH 5 and a local minimum may have been observed near pH 6. This pH dependence is in general agreement with that of Levin [11] regarding increased leaching of radium from mine tailings below pH 5. The weak pH dependence between pH 5 and

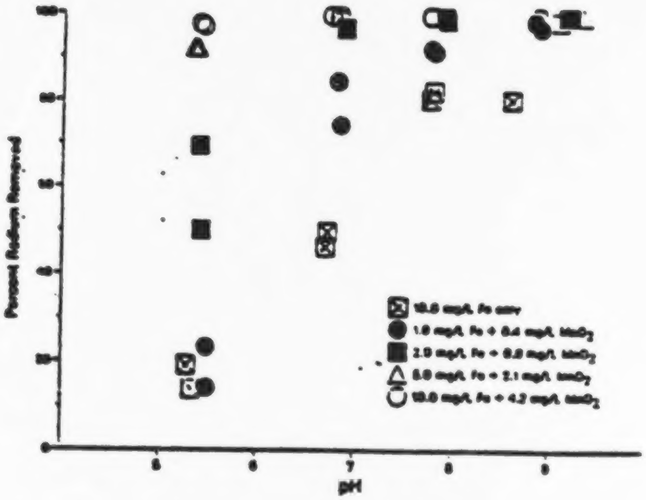

Figure 22. Radium removal in sodium form synthetic water by mixed iron/manganese oxides. Permanganate sufficient to oxidize 90% of the iron added. Ra = 32 pCi/L

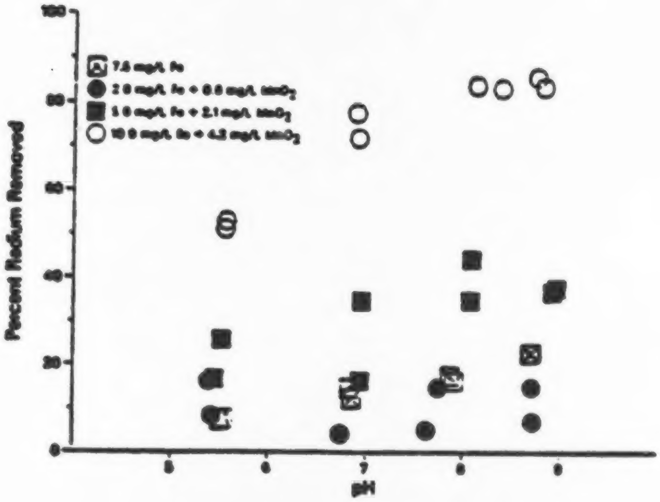

Figure 23. Radium removal in Oxford water by mixed iron/manganese oxides. Permanganate sufficient to oxidize 90% of the iron added. Ra = 32 pCi/L

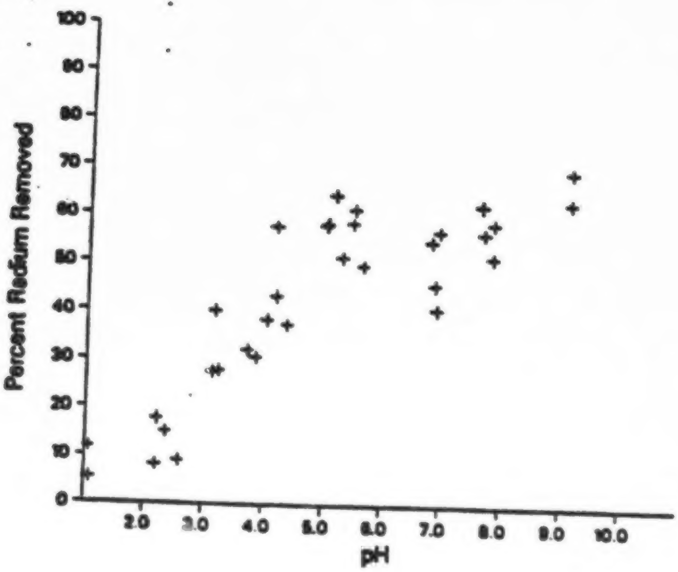

Figure 24. Percent radium removed in Na-Form synthetic water by acid washed sand as a function of pH. Sand = 10 g/L, Ra = 48 pCi/L

9 suggest that a process based on sorption to filter sand would not be very sensitive to normal pH variation encountered in drinking water (pH 6.5 to 8.5).

Percent Ra-226 sorbed was not a function of radium concentration, but sorption increased as sand concentration increased as shown in Figure 25. The results are consistent with a linear isotherm characterized by a distribution coefficient of approximately 0.24 L g^{-1} at pH 8.2 in Na-form water as shown in Figure 26.

Effect of Hardness on Sorption to Filter Sand --

Sorption to 50 g/L filter sand was depressed from approximately 80% in the absence of hardness to approximately 60% in the presence of either 6mMCa or 6mMMg (600 mg/L as $CaCO_3$ for both Ca and Mg) as shown in Figure 27.

Percent radium removed from Oxford water was not a function of total dosed R-226 (Figure 28) which is again consistent with a linear isotherm.

Removals were also comparable in both Oxford and Eldon water as a function of sand dosage. Percent removals determined in Oxford and Eldon water as a function of sand concentration were also comparable to those obtained in synthetic groundwater containing significant hardness. Linear isotherms at approximately pH 7.1 for Oxford, Eldon and synthetic water containing 6 mM Ca (Figure 29) or at pH 8.7 for Oxford and synthetic water containing 6 mM Ca and 6 mM mg were nearly identical (Figure 30) which indicated that behavior in synthetic water closely resembles that in real waters if hardness is comparable.

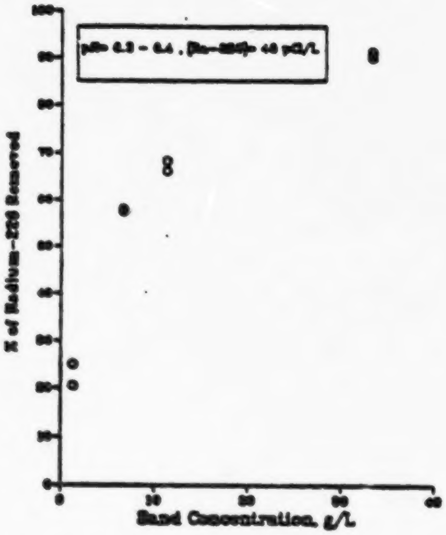

Figure 25. The effect of sand concentration on radium removal at pH 8.3 - 8.4 in sodium form synthetic water Ra-226 = 48 pCi/L

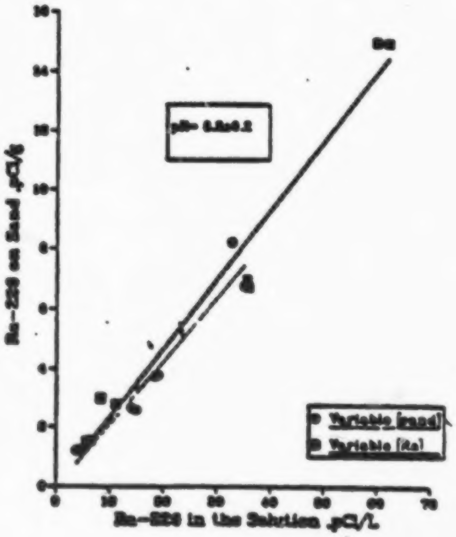

Figure 26. Radium sorbed on sand vs radium concentration remaining in solution. Sodium form synthetic water at pH 8.2

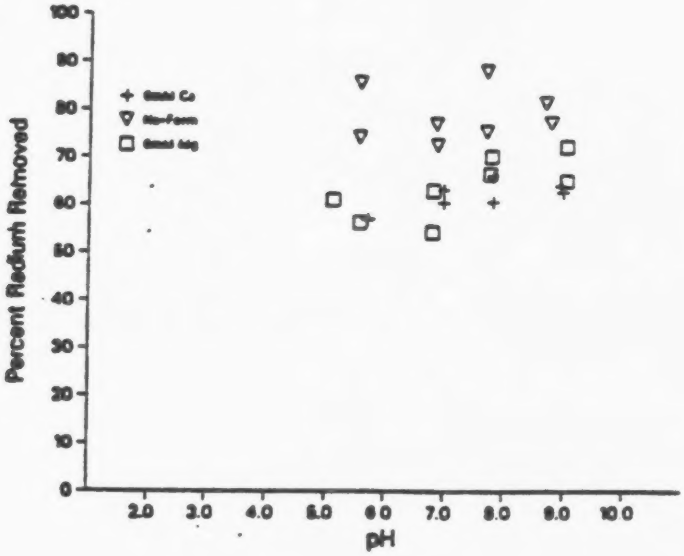

Figure 27. Percent radium removed on acid washed sand as a function of pH: 6 mM Ca-Form vs 6 mM Mg vs Na-Form synthetic water. Sand = 50 g/L, Ra = 48 pCi/L

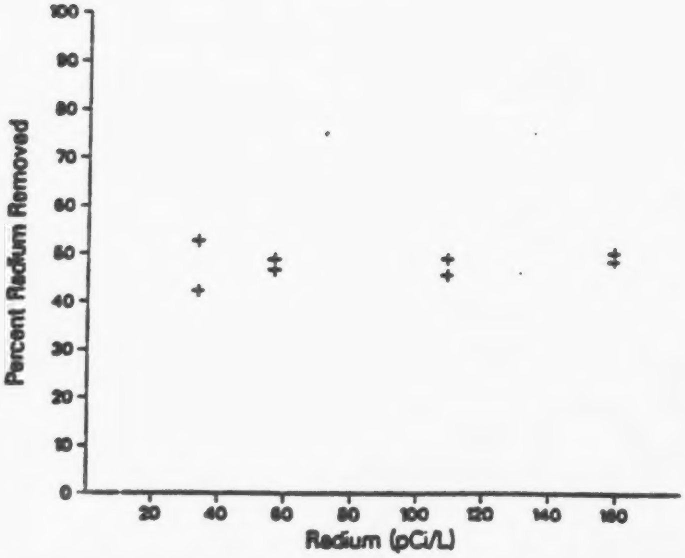

Figure 28. Percent radium removed as a function of radium concentration at pH 7.1 in Oxford water (8.5 mM ca, 4.1 mM Mg). Sand = 50 g/L

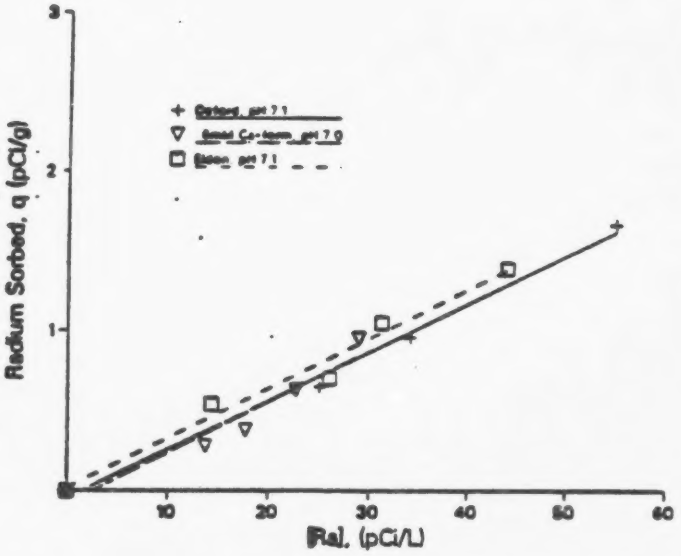

Figure 29. Comparison of radium adsorption isotherms (Sand) developed in Eldon, Oxford and 6 mM Ca-Form synthetic waters at pH 7.1

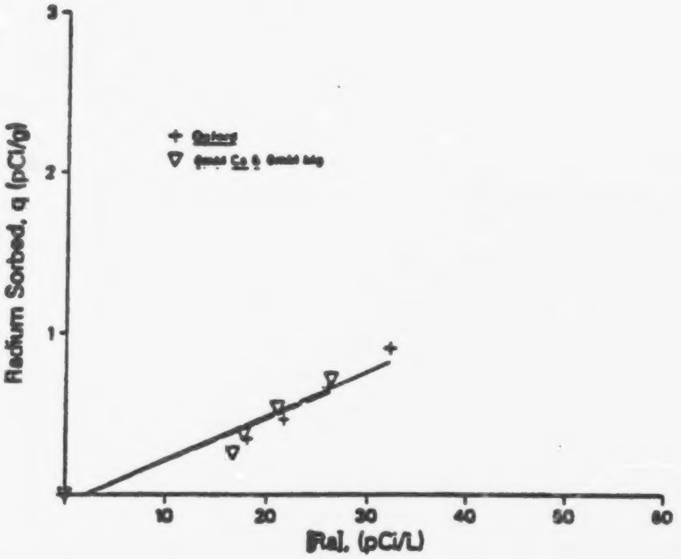

Figure 30. Comparison of radium adsorption isotherms (Sand) developed in Oxford and 6 mM Ca + 6 mM Mg-Form synthetic waters at pH 8.7

Regeneration of Filter Sand

Pilot Plant Studies --

Pilot plant studies were conducted to investigate the potential of using filter sand as an acid regenerable media in the presence of 2 mg/L added Fe and approximately 80 pCi/L of added Ra-226. A dilute acid of 4 empty bed volumes at a loading rate of 3 gpm/ft^2, the same as the filtration rate was used. Under these conditons the acid volume used was about 0.3% of the total volume of treated water. A daily rinse using 0.1 N HCl (pH 1) as a regenerant decreased effluent radium concentration from about 50 pCi/L to approximately 10 pCi/L (Figure 31). Similar results were obtained when a 0.01 N (pH 2) dilute acid rinse was used as shown in Figure 32. Acid cost for pH 2 would be only 1/10 of pH 1, a significant savings.

Cumulative Ra-226 recovery in both 0.1 and 0.01 N HCl rinse is shown in Figure 33 and indicated the efficiency of radium recovery as a function of both time and acid concentration.

Figure 33 also shows that only iron is removed by prior backwash and therefore the radium that was recovered must be associated with the sand and not the iron.

Figure 34 shows that a loading rate below 4 gpm/ft^2 is necessary for maximum radium sorption onto filter sand for water hardness of 400 mg/L as $CaCO_3$. Another test at 100 mg/L as $CaCO_3$ water hardness showed that loading rates up to 12 gpm/ft^2 did not reduce radium sorption significantly.

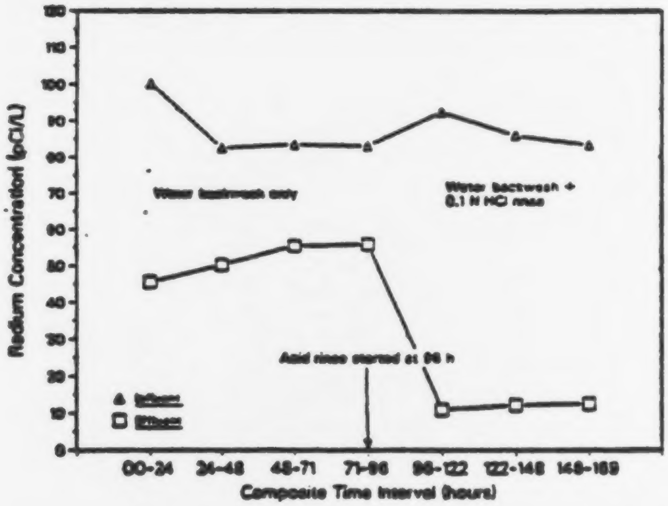

Figure 31. Radium removal in the UHL pilot plant showing effect of a daily pH 1 HCl rinse. Hardness = 150 mg/L, as $CaCO_3$, Fe = 2.0 mg/L, pH = 7.5

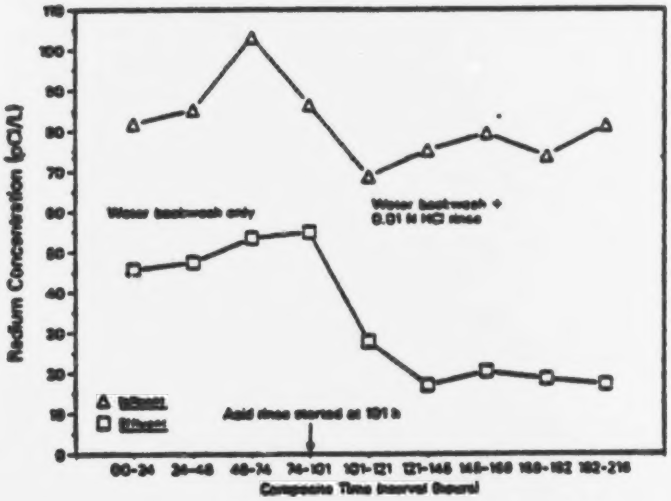

Figure 32. Radium removal in the UHL pilot plant showing effect of a pH 2 HCl rinse during daily backwash. Hardness = 150 mg/L, as $CaCO_3$, Fe = 2.0 mg/L, pH = 7.5

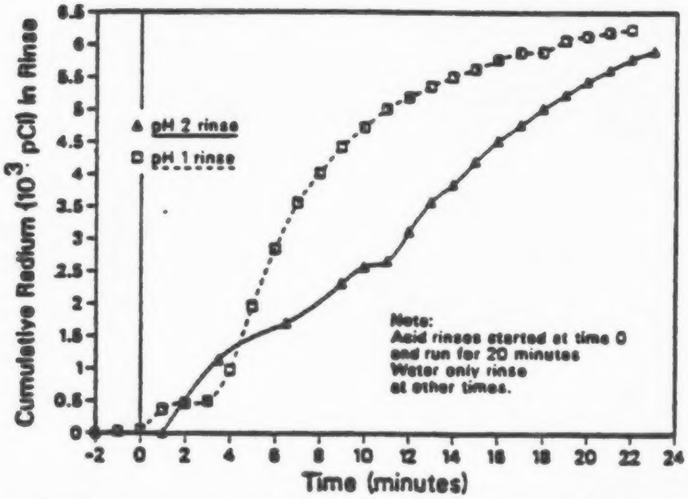

Figure 33. Comparison of cumulative radium recovered in pH 1 and pH 2 regenerant rinses. Regenerant loading rate 7.4 m/h (3 gpm/ft^2), 4 bed volumes used, EBCT 5 minutes. Regenerant flow rate 1 L/min.

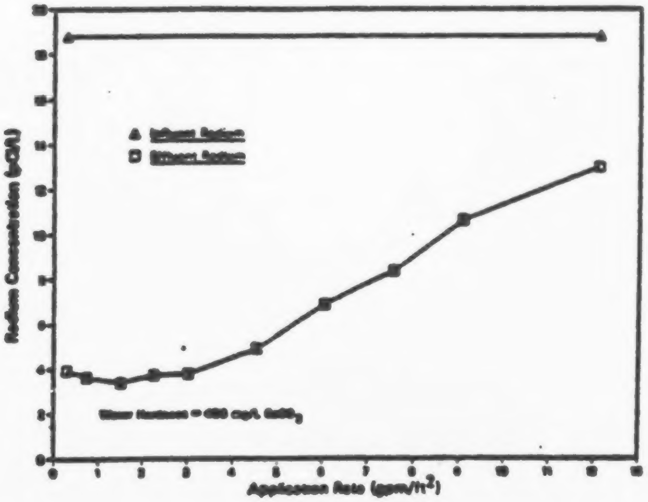

Figure 34. Radium concentration profiles as a function of loading rate. Initial pH 1 rinse. Total hardness 400 mg/L as CaCO$_3$.

Field Studies at Oxford, Iowa (Sand Filter Effluent) --

Figure 35 shows influent/effluent radium concentration profiles when 4 bed volumes of 0.1 N HCl (pH 1) regenerant was used daily for two cycles utilizing a water loading rate of 3 gpm/ft^2. Effluent radium concentration decreased to approximately 3 pCi/L from an influent value of about 8 to 11 pCi/L. Upon termination of the acid regeneration, radium removal decreased significantly.

Significantly better performance was observed when the loading rate was decreased to 1.5 gpm/ft^2 as shown in Figure 36 which shows effluent radium concentration of only about 1 to 2 pCi/L.

Radium removal efficiency decreased significantly from an initial value of 60% when pH 2 regenerant was used to 25 to 35% when pH 3 regenerant was used (Figure 37).

One possible explanation of the decreasing efficiency with time could be that iron precipitates are gradually coating the sand. The solubility of ferric hydroxides also decreases greatly as pH is increased from 1 to 3.

Field Studies at Oxford, Iowa (Aerator Effluent) --

An experiment was conducted over a period of approximately 13 days which investigated removal of radium by sand sorption from the effluent of the aeration tank at the city of Oxford (simultaneous radium and iron removal) as a function of type and flow rate of acid regenerant. Influent water flow rate was fixed (1.5 gpm/ft^2). The concentration of iron in the influent was approximately 0.5 mg/L and was reduced to approximately 0.08 mg/L after passage through the experimental radium removal filter. Radium removal in the presence of significant iron

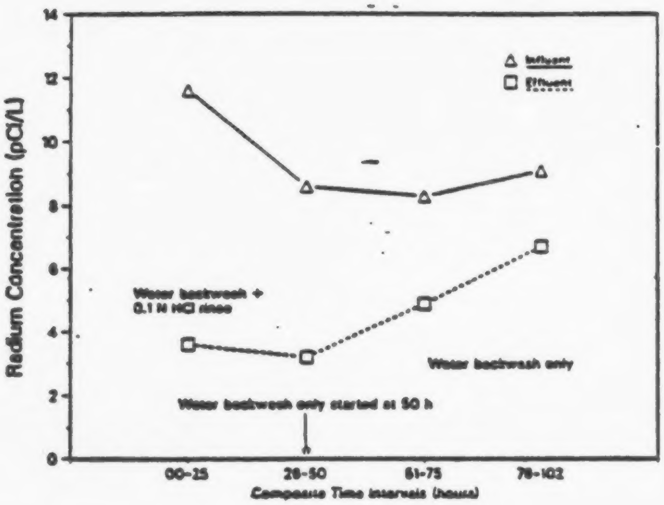

Figure 35. Ra Concentration profiles in Oxford Water. With and without pH 1 (0.1 N HCl) regeneration. Loading rate 3 gpm/ft^2.

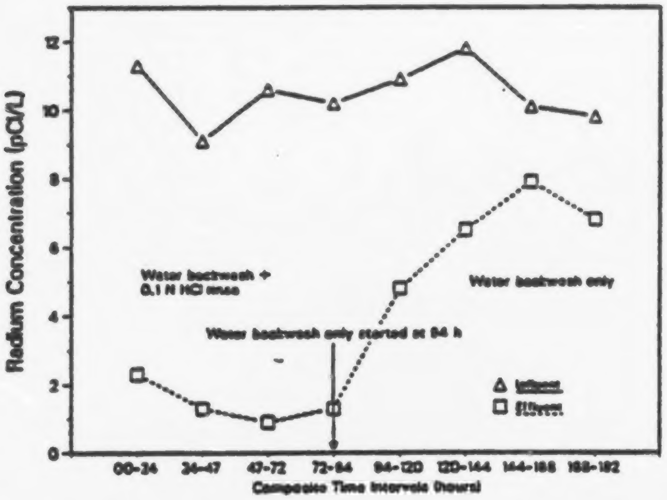

Figure 36. Ra Concentration profiles in Oxford water. With and without pH 1 (0.1 N HCl) regeneration. Loading rate 1.5 gpm/ft^2.

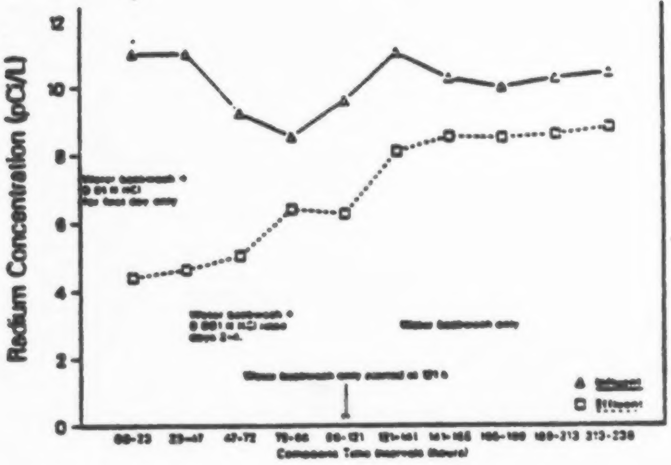

Figure 37. Ra concentration profiles in Oxford water.
With and without pH 3 (0.001 N HCl) regeneration.

flocs was only about 25 - 35% (Figure 38) compared with 80 - 90% removals obtained when the existing sand filter effluent (absence of significant iron flocs) was filtered and periodically regenerated. Removals were similar with both dilute sulfuric acid and dilute hydrochloric acid rinses, and were similar at 1.5 gpm/ft^2 and a 3.0 gpm/ft^2 regenerant loading rates.

The large reduction in performance observed when simultaneous iron and radium removal was practiced was not expected based on previous laboratory batch and pilot plant results which indicated little iron floc interference. The mechanism by which the presence of iron flocs inhibited radium removal is not clear. While it may be supposed that the flocs coated the sand thereby blocking radium sorption, it must be noted that most of the iron flocs were probably removed in the first few inches of sand bed as indicated by visible color changes. Therefore, significant amounts of "clean" sand probably existed below the iron floc removal zone even after one day of operation. Possibly the influent may have contained significant (with respect to radium) concentrations of unoxidized soluble ferrous iron which effectively competed for sorption sites below the zone in which most of the iron floc was removed.

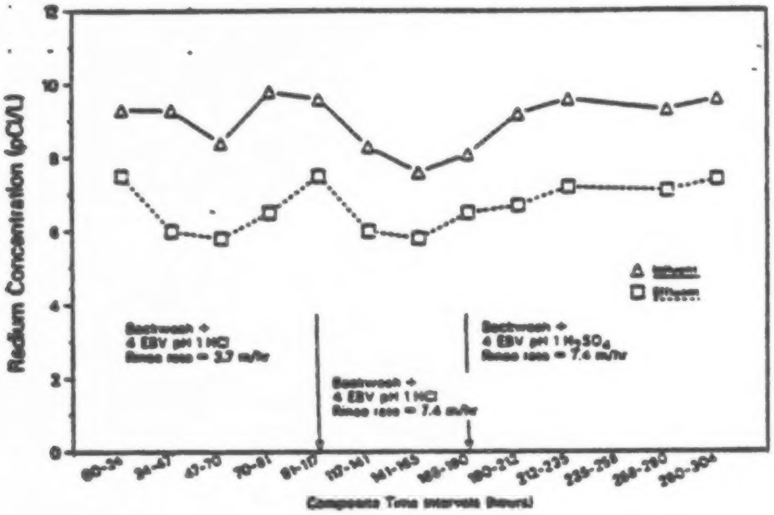

Figure 38. Influent and effluent Ra-226 concentration profiles. Treatment of Oxford aeration tank effluent. Comparison of sulfuric and hydrochloric acid regeneration at two regenerant loading rates.

SECTION 6.

MANGANESE DIOXIDE COATED FILTERS

(North Carolina State University Study)[12]

SUMMARY OF MANGANESE DIOXIDE COATED FILTERS

A process was developed for coating woven acrylic cartridge filters with manganese dioxide (MnO_2). The coating process consists of circulating hot potassium permanganate ($KMnO_4$) through the filter. The investigator surmises that the acrylic filter material is oxidized and the $KMnO_4$ reduced; resulting in MnO_2 that adheres to the filter. Both loose fiber and woven filters averaged 22.5 percent MnO_2 by weight or 56.25 grams MnO_2 in a ten-inch long 250 gram filter element.

The manganese dioxide coated filters were tested for radium removal from waters with high and low hardness. Bleed stream testing of the ten-inch MnO_2 filter on high hardness water containing a total radium concentration of 36.4 pCi/L resulted in treating 800 ft^3 of water before the effluent radium concentration reached 5 pCi/L. Total filter capacity was exhausted after treating 5500 ft^3 of water. A total of 801 nanocuries of total radium were removed or 14.2 nanocuries per gram of MnO_2. The removal efficiency from the first 800 ft^3 of water was 86%. Bleed stream testing of the ten-inch MnO_2 filter on low hardness water containing a total radium concentration of 13.2 pCi/L resulted in treating greater than 1000 ft^3 of water before the effluent concentration reached 5 pCi/L. Total filter capacity was exhausted after treating 3000 ft^3 of water. A total of 290 nanocuries of total radium were removed or 5.2 nanocuries per gram of MnO_2. The removal efficiency for the first 1000 ft^3 of water was 66%.

Dilute solutions of the metals cadmium, calcium, cesium, chromium, cobalt, iron manganese and sodium were tested to determine their sorption onto the MnO_2 filter. Results revealed a positive uptake of metals. The greatest was the uptake of cadmium. Results showed that no chromium was taken up by the MnO_2 filter.

Testing confirmed that no organic acrylonitrile or acrylic fiber were leached off the filter into the product water. No manganese was detected leaching off the filter into the product water.

MANGANESE DIOXIDE COATING PROCESS

The woven acrylic cartridge filters were coated with manganese dioxide as shown in Figure 39. Hot potassium permanganate solution at 55 to 58°C was pumped through two acrylic cartridge filters in series at a flow rate of 8 t 10 GPM. It takes approximately twelve hours for both filters to become saturated with manganese dioxide. After the coating process, the filters were rinsed with tap water for twenty minutes in both directions until no excess manganese was leaching into the rinse water. The prepared filters were then packaged and sealed in plastic bags containing a one mg/L solution of potassium permanganate to inhibit biological growth. The quantity of MnO_2 that was coated onto the filters was approximately 22 1/2% of the total filter weight including MnO_2. It is the investigator's opinion that the acrylic filter surface is oxidized and the $KMnO_4$ reduced such that MnO_2 adheres to the filter and the potassium salts are washed away.

BLEED STREAM FIELD TESTS (RADIUM SORPTION)

A high hardness high pH water (Highland Park) and a low hardness low pH water (Gateway) were tested for radium removal with ten-inch woven acrylic filter elements. The raw water analysis for both waters

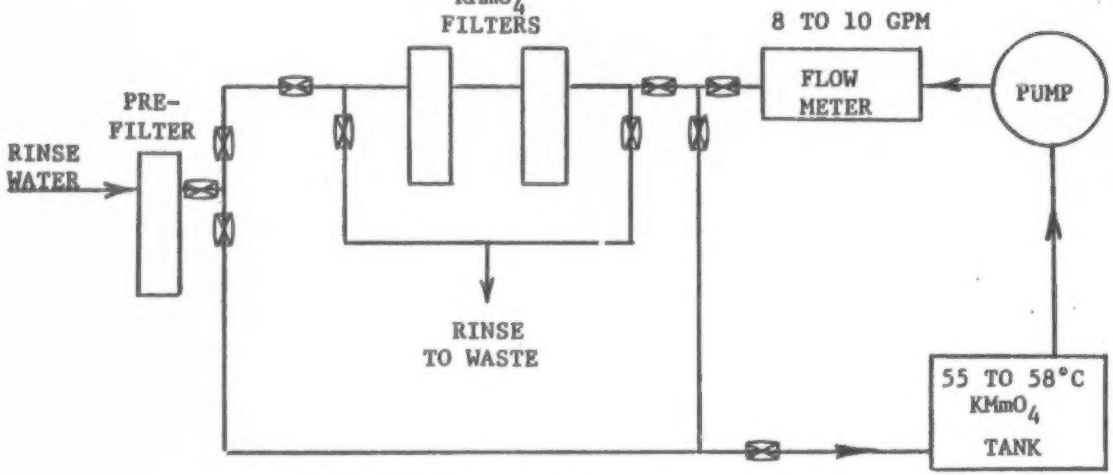
KMmO$_4$
FILTERS
8 TO 10 GPM
PRE-
FILTER
FLOW
METER
PUMP
RINSE
WATER
RINSE
TO WASTE
55 TO 58°C
KMmO$_4$
TANK

Figure 39. Schematic diagram of process for coating woven acrylic cartridge filters with MmO_2.

is given in table 18.

Bleed stream testing of the MnO_2 filter in the Highland Park Water System resulted in a decrease in total radium, from the influent concentration of 36.4 pCi/L total radium (see Table 19). One ten-inch MnO_2 fiber filter element treated a volume of approximately 800 cubic feet of water, at a flowrate of 3 gallons per minute, before the effluent radium concentration increased to a level of 5 pCi/l Total breakthrough was reached after approximately 5500 cubic feet of water was treated (Table 19). The single ten-inch filter element of approximately 250 grams MnO_2 fiber, contained 56.25 grams of MnO_2, and 193.75 grams of acrylic fiber. This accounted for the removal of 801 nanocuries total radium, or 14.2 nanocuries per gram of MnO_2, at a removal efficiency of greater than 86 percent from the first 800 cubic feet of water treated. Total breakthrough occurring after approximately 5500 cubic feet of water treated was preceeded by the uptake of 2076 nanocuries total radium, or 36.9 nanocuries per gram of MnO_2.

Bleed stream testing of the MnO_2 filter in the Gateway Water System resulted in a decrease in total radium, from the influent concentration of 13.2 pCi/L total radium (see Table 20). A single ten-inch MnO_2 fiber filter element treated a volume of approximately 1000 cubic feet of water, at a flow rate of 3 gallons per minute, before the effluent concentration increased to a level of 5 picocuries per liter. Total radium breakthrough was reached after approximately 3700 cubic feet of water was treated (Figure 20).

Table 18. RAW WATER ANALYSIS FOR HIGHLAND PARK AND GATEWAY*

Parameter	High Hardness Highland Park	Low Hardness Gateway
Total Radium (pCi/L)	36.4	12.3
Total Hardness (mg/L as $CaCO_3$)	227	23
Calcium (mg/L)	74.6	2.4
Sodium (mg/L)	110.8	5
Alkalinity (mg/L)	124	0
Chloride (mg/L)	203	0
Total Dissolved Solids (mg/L)	590	54
Turbidity	0.2	0.05
Magnesium (mg/L)	9.8	4.1
pH	7.8	4.5
Arsenic (mg/L)	< 0.01	< 0.01
Barium (mg/L)	0.32	< 0.10
Cadmium (mg/L)	< 0.005	< 0.005
Chromium (mg/L)	< 0.01	< 0.01
Fluoride (mg/L)	1.04	< 0.10
Lead (mg/L)	< 0.03	< 0.03
Mercury (mg/L)	< 0.0002	< 0.0002
Nitrate (mg/L)	< 0.05	5.65
Selenium (mg/L)	< 0.005	< 0.005
Silver (mg/L)	< 0.02	< 0.05
Iron (mg/L)	< 0.05	< 0.05
Manganese (mg/L)	< 0.03	< 0.03

*Analysis performed by N. C. State Laboratory of Public Health

The single ten-inch filter element of approximately 250 grams MnO_2 fiber (56.25 grams MnO_2) removed 290 nanocuries total radium, or 5.2 nanocuries per gram MnO_2 at a removal efficiency of greater than 66 percent from the first 1000 cubic feet of water treated. Total breakthrough occurred after approximately 3000 cubic feet of water was treated, and was preceeded by a total uptake of 439 nanocuries total radium, or 7.8 nanocuries per gram of MnO_2.

TABLE 19. BLEED STREAM FIELD TEST, MnO_2 FILTRATION (HIGHLAND PARK)*

Total Flow ($ft.^3$)	Ra-226 (pCi/L)	Ra-228 (pCi/L)	Total Effluent Radium (pCi/L)
0.5	0.26	0.37	0.63
2.0	0.31	0.44	0.75
12.0	0.46	0.66	1.12
48.0	0.31	0.44	0.75
440.5	0.71	1.01	1.72
526.1	0.97	1.34	2.28
1106.9	3.74	5.33	9.07
1163.2	2.99	4.26	7.25
1738.7	5.66	8.06	13.72
2157.1	6.19	8.82	15.01
2401.1	9.11	12.98	22.09
3051.8	10.93	15.57	26.50
3740.0	12.29	17.51	29.80
4045.3	12.35	17.59	29.94
4587.8	13.93	19.84	33.77
5271.0	13.95	19.87	33.82

* Total influent radium concentration = 36.4 pCi/L

TABLE 20. BLEED STREAM FIELD TEST, MnO_2 FILTRATION (GATEWAY)*

Total Flow ($ft.^3$)	Ra-226 (pCi/L)	Ra-228 (pCi/L)	Total Effluent Radium (pCi/L)
1.0	1.01	0.07	1.08
2.4	0.91	0.07	0.98
12.1	1.03	0.07	1.11
48.3	0.98	0.07	1.05
142.4	1.22	0.09	1.31
701.4	3.04	0.22	3.25
1208.0	5.46	0.39	5.85
1758.7	7.72	0.55	8.27
2300.6	9.87	0.70	10.57
2806.6	11.91	0.85	12.76
3647.4	12.08	0.86	12.93

* Total influent radium concentration = 13.2 pCi/L

Bleed stream testing of MnO_2 fiber in the Highland Park Water System resulted in the removal of 36.9 nanocuries per gram of MnO_2 fixed on acrylic fiber base. Bleed stream testing of the Gateway Water System resulted in the removal of 7.8 nanocuries per gram of fixed MnO_2. The water quality parameters for the Highland Park and Gateway Water Systems are listed in Table 18. The difference in the pH of these water sources was the most significant water quality parameter. The Highland Park water had a pH of 7.8, while Gateway's water had a pH of 4.5. An increase in pH increases the ability of MnO_2 to sorb cations due to the higher adsorption energy. This correlation of pH is evidenced in the increased level of radium uptake per gram MnO_2 of the Highland Park system. The bleed stream test at the Highland Park Water System had a measured radium uptake per gram MnO_2 of 4.7 times greater than the uptake measured at the Gateway Water System. The higher calcium concentration of the Highland Park water would compete with radium for adsorption sites on the MnO_2 but it appears that the pH difference had a greater affect on radium sorption than the increased calcium.

SORPTION OF OTHER METALS ONTO MANGANESE DIOXIDE

Bench-top testing of the MnO_2 fiber was performed for removal of radium, cadmium, calcium, cesium, cobalt, iron, and manganese.

A 53.5 gallon water sample from the Highland Park Water System, containing 36.4 picocuries total radium per liter, was pumped through a loose MnO_2 fiber filter containing 3.38 grams MnO_2. A level of uptake of 7.37 nanocuries total radium per gram MnO_2 was achieved. However. the radium removal efficiency of 100 percent was maintained throughout the test. a significant level of uptake while performing at a high level of radium removal.

Dilute solutions of metals, alone and in combination with other metals were pumped through a column or columns containing loose MnO_2 fiber. The breakthrough results are listed in Table 21. From the amount of metal uptake on MnO_2 a comparison of the adsorption potential can be made for each metal and combination of metals. In each of these cases a significant amount of metal was removed by adsorption onto MnO_2, showing the potential of competition with radium for sorption sites. For the cations listed in Table 21, calcium would usually be present in the highest concentration and the table indicates moderate preference for calcium as compared to the other cations.

TABLE 21. METAL REMOVAL WITH MnO_2 COATED FIBER

Metal	Concentration (mg/L)	MnO_2 (grams)	Metal Uptake (mg metal)	Metal Uptake (mg/g MnO_2)	1/2 Breakthrough (liters)	Breakthrough (liters)
Cadmium	2.0	3.825	700	183.01	240	350
Calcium	2.2	5.175	275	53.14	62	125
Calcium	2.2	10.575	550	52.01	140	250
Cesium	10.0	12.375	2000	161.62	150	200
Cesium	10.0	12.375	2000	161.62	165	200
Cobalt	3.0					
Sodium	1.0					
Cesium	10.0	16.2	1230	75.93	85	123
Cobalt	3.0					
Cesium	10.0	13.95	2870	205.73	190	287
Sodium	1.0					
Cobalt	2.8	14.4	1680	116.67	250	600
Cobalt	4.4	3.375	440	130.37	30	100
Cobalt	4.4	6.75	1000	162.96	82	250
Cobalt	2.8	11.7	910	77.78	200	325
Cesium	10.0					
Sodium	3.5					
Cobalt	3.1	11.025	775	70.29	90	250
Cesium	10.0					
Cobalt	3.5	26.1	2275	87.16	460	650
Sodium	3.5					
Iron	4.15	3.375	1037.5	307.41	45	250
Iron	4.15	6.67	1245	186.66	125	300
Manganese	4.15	3.6	830	230.55	70	200
Manganese	4.15	7.2	996	138.33	170	240

SECTION 7

EVALUATION OF RADIUM REMOVAL AND WASTE DISPOSAL SYSTEM FOR SMALL COMMUNITY WATER SUPPLY

(Rocky Mountain Consultants, Inc., Denver, Colorado)[13]

SUMMARY (Iron Removal, Ion Exchange, Waste Disposal)

A full scale well water treatment plant for a small community was evaluated for radium removal. The plant consists of iron removal with aeration, filtration and settling; hardness and radium removal with ion exchange; and radium removal from the waste brine with the Dow radium selective complexer (RSC). The purpose of this research was to determine the effectiveness of each stage for radium removal. Results showed that very little radium was removed across the iron removal process. Radium was removed to concentrations below the MCL with ion exchange and as expected, hardness broke through before radium. Greater than 99% of the radium was removed from the waste brine by the RSC. Results given here are not final because the project will not be completed until October, 1987.

DISCUSSION

General Information

Data was obtained to assess the effectiveness of the overall treatment plant operation. The treatment plant consisted of iron removal through aeration, settling and filtration; hardness and radium removal through ion exchange and waste brine treatment for radium removal through the Dow radium selective complexer. Arrangements were made to send the spent complexer resin to a radiological disposal site in Nevada at a nominal cost. The complexer resin occupies a volume of approximately 31 gallons and has been treating the waste brine for six months, to date, without breakthrough. This project is still going on and, therefore, final breakthrough capacity remains to be determined. This is a full scale treatment plant for a small community in Colorado.

Iron Removal

Table 22 shows that the raw water radium concentration varied from approximately 27 to 35 pCi/L and the effluent from the Water Boy unit varied from approximately 22 to 35 pCi/L. This verifies the information in section 5 which states that very little radium removal takes place across the iron removal process. Potassium Permanganate was added before the Water Boy (iron settling and filtration unit) but it was not enough to oxidize all the iron. Therefore, there was ferrous ion left that used the adsorption sites on the manganese dioxide instead of radium. For this plant, the intention was to remove all radium with ion exchange and not with iron removal so that waste brine containing radium could be treated with the Dow complexer.

TABLE 22. REDHILL FOREST WATER QUALITY MONITORING DATA - GENERAL TREATMENT PLANT OPERATION

Sample Location and WQ Parameters	Date									
	9/10/86	9/10/86	9/12/86	9/14/86	9/14/86	9/16/86	9/18/86	9/18/86	9/21/86	9/21/86
I. RAW WATER Sample ID (into plant)	RW910-A	RW910-B	RW912-C	RW914-D	RW914-E	RW916-F	RW918-G	RW918-H	RW921-I	RW921-J
Iron (mg/L)	7.3	6.3	6.49	5.54	6.60	6.11	8.26	6.11	3.19	6.71
Manganese (mg/L)	0.43	0.42	--	--	--	0.40	--	--	--	0.38
Sodium (mg/L)	16.1	8.05	--	--	--	10.8	--	--	--	6.79
Hardness (mg/L)	335	245	336	263	225	281	316	241	265	249
Total Solids (mg/L)	--	--	428	--	--	--	--	--	--	340
Radium 226 (pCi/L)	30±6	27±6	33±7	31±6	32±6	32±6	32±7	30±6	33±7	35±8
III. TREATED WATER Sample ID (Effluent Ion Exchange)	IXE910-A	IXE910-B	IXE912-C	IXE914-D	IXE914-E	IXE916-F	IXE918-G	IXE918-H	IXE921-I	IXE921-J
Iron (mg/L)	0.11	0.20	0.20	0.27	0.39	0.28	0.39	0.96	1.00	1.62
Manganese (mg/L)	.01	0.01	--	--	--	0.07	--	--	--	1.12
Sodium (mg/L)	147	121	118	86.4	384	137	95.7	65.6	33.2	15.7
Hardness (mg/L)	10	10	22	70	28	17	22	108	207	238
Total Solids (mg/L)	--	--	432	--	--	--	--	--	--	428
Radium 226 (pCi/L)	4±2.5	3.8±2.6	0.3±1.7	3.6±2.6	3.7±2.7	0±1.4	0.6±1.9	4.7±3.0	12±4	13±4

TABLE 22. REDHILL FOREST WATER QUALITY MONITORING DATA - GENERAL TREATMENT PLANT OPERATION (Contd)

Sample Location and WQ Parameters	Date									
	9/10/86	9/10/86	9/12/86	9/14/86	9/14/86	9/16/86	9/18/86	9/18/86	9/21/86	9/21/86
II. EFFLUENT FROM* WATERBOY UNIT Sample ID	WBE910-A	WBE910-B	WBE912-C	WBE914-D	WBE914-E	WBE916-F	WBE918-G	WBE918-H	WBE921-I	WBE921-J
Iron (mg/L)	0.48	2.5	0.89	1.27	4.27	1.70	1.77	4.49	2.05	5.22
Manganese (mg/L)	0.60	0.94	--	--	--	1.29	--	--	--	1.24
Sodium (mg/L)	--	--	--	--	--	--	--	--	--	--
Hardness (mg/L)	212	240	292	252	246	307	254	247	277	261
Total Solids (mg/L)	--	--	--	--	--	--	--	--	--	--
Radium 226 (pCi/L)	22±5	25±6	28±6	28±6	29±6	28±6	22±6	26±6	35±8	29±7
IV. VOLUME TREATED SINCE LAST BACKWASH										
A. Ion Exch. Sys(Unit 1)	0	10,000	20,000	30,000	0	10,000	20,000	30,000	40,000	50,000
B. Water Boy Unit	0	10,000	20,000	30,000	40,000	50,000	60,000	70,000	80,000	90,000

*Water boy unit includes $KMnO_4$ addition, settling and filtration for iron removal.

NOTE: From 9/10/86 through 9/21/86 an intensive monitoring of plant operation was conducted with samples collected after every 10,000 gallons were treated.

Ion Exchange

The purpose of the intensive monitoring during the treatment cycles given in Table 22 was to determine approximately when radium breakthrough occurs in relation to hardness breakthrough for the ion exchange process. As can be seen from the data in Table 22, the raw water hardness varies with time, and affects the length of the treatment runs between regeneration cycles for the ion exchange process. Table 22 shows that radium begins to break through when the accumulated volume of water treated in the ion exchange process exceeds 30,000 gallons and elevated radium in the effluent occurred at 40,000 gallons. Previously, the volume of water treated for the ion exchange process between backwash operations has been between 50,000 and 60,000 gallons, however, it appears, based upon the above results (Table 22), that backwashing should be performed more frequently, probably every 30,000 to 40,000 gallons.

The resin volume is approximately 224 gallons and therefore 134 to 179 bed volumes could be treated before regeneration. It was shown in section 4 of this report that cation exchange resins prefer radium over hardness. The data in table 22 also verifies that the resin has preference for radium over hardness, but table 22 also indicates that radium breakthrough occurs shortly after hardness breakthrough. This is seen in the 9/18/86 Column where hardness increased from 108 to 207 mg/L as $CaCO_3$ and radium-226 increased from 4.7 to 12 pCi/L. This indicates that after many cycles of operation radium accumulates on the resin and this explains why radium breaks through shortly after hardness. This was also shown in section 4 with data for virgin resins compared to data taken after repeated cycles.

Waste Brine Treatment With Radium Selective Complexer

The data presented in Table 23 clearly shows that the RSC is truly radium selective. In general, the concentration of the other constituents analyzed (i.e., iron, manganese, sodium, hardness, and total solids) are virtually unchanged in passing through the RSC tank. However, in excess of 99% of the influent radium is removed and composited in the RSC. A check was recently made of the condition of the RSC in regard to solids buildup in the inflow side and minor accumulations were observed. The flow rate through the RSC has been, and is, maintained at about 23 gpm when the system is operating. This flow rate is equivalent to a bed surface loading rate of about 10.5 gpm/ft^2. With the current bed depth of 24 inches, the average contact time of the inflow wastewater with the RSC is about 1.4 minutes.

Most of the radium in the raw water coming into the plant is removed by the ion exchange process and is subsequently complexed in the RSC when the regeneration waste brine is treated by the RSC. The RSC has a resin volume of 31 gallons and, therefore, 471 BV (14,600/31) of waste brine were treated from September 10 through September 29, 1986. The RSC was still removing over 99% of the radium from the waste brine on December 10, 1986 and over 31,700 gal or 1023 BV of waste brine had been treated.

The complexer can either be installed at the influent to the ion exchange system to treat the potable water or on the waste brine. When installed on the waste brine, the complexer will treat a much smaller volume of water at a much higher dissolved solids and higher radium concentration. One purpose of this research is to determine which RSC location would be the most cost effective and result in the easiest handling of the final radium for disposal. As mentioned above, 1023 BV of waste brine has been treated. During this time the 1,463,000 gallons of drinking water has been treated. If this volume of water were treated by the 31 gallons of complexer it would equal 47,194 BV. A larger vessel and much more RSC would be required to treat the potable water, therefore, the process would be more expensive if the RSC were used to treat the total water supply. The capacity of the RSC when used on potable water vs. waste brine still needs to be determined.

TABLE 23. SUMMARY OF WQ DATA FOR REGENERATION WASTEWATER THROUGH RSC RESIN

			PARAMETERS						
Date	Accumulated Volume Treated Gals.	Sample ID	Iron mg/L	Manganese mg/L	Sodium mg/L	Hardness ($CaCO_3$) mg/L	Solids mg/L	Total Radium pCi/L	% Radium Removal
7/10/86	0	A(Inflow)	2.48	23.8	11,600	476	34,900	860±30	
		B(Outflow)	0.98	16.7	13,300	245	34,600	16±11	98.1
7/10/86*	0	B(Inflow)	2.39	24.8	12,000	494	35,600	870±30	
		B(Outflow)	1.42	23.2	12,100	440	35,300	15±11	98.3
7/30/86	2,400	(Inflow)	2.03	31.8	11,000	9,850	41,700	1280±40	
		(Outflow)	1.56	32.2	11,000	10,200	41,800	1.6±3.2	99.9
8/18/86	6,335	(Inflow)	5.61	30.6	11,600	10,500	44,400	1460±50	
		(Outflow)	4.91	30.2	11,500	12,000	44,600	7.1±5.1	99.5
8/25/86	7,000	(Inflow)	8.0	29.9	12,100	10,200	50,300	1260±40	
		(Outflow)	6.8	29.7	12,000	10,100	49,500	7.8±3.2	99.4
8/31/86	9,460	(Inflow)	9.0	33.1	12,600	11,500	54,200	1400±40	
		(Outflow)	8.5	33.1	12,700	11,600	55,200	9.4±3.5	99.3
9/23/86	13,430	(Inflow)	5.08	21.0	11,700	7,830	41,700	1200±100	
		(Outflow)	4.61	21.0	11,800	7,770	42,500	6.0±3.2	99.5
9/29/86	14,600	(Inflow)	7.21	30.5	11,400	8,350	37,600	920±30	
		(Outflow)	7.15	31.5	11,500	8,420	37,600	4.1±2.4	99.6
Averages for samples collected for period 7/10/86 through 9/29/86 (7 samples) excluding B samples collected on 7/10/86									
		Inflow	5.64	28.7	11,710	8,390	43,540	1197	
		Outflow	4.93	27.8	11,970	8,620	43,690	7.4	99.4

Accumulated Flow = 14,600 gals.
RSC resin was replaced on 7/10/86
* Q=11.0 gpm all other samples collected are for a flow of 23 gpm through the RSC tank.

SECTION 8

OTHER RADIUM REMOVAL PROCESSES

LIME & LIME-SODA SOFTENING

The literature[14] shows that lime and lime soda ash softening have been demonstrated on a full-scale plant level to achieve 75-96 percent removal of radium. Radium carbonate and radium sulfate are listed[15] as being insoluble in water, but at the very low concentrations around the drinking water regulation MCL of 5 pCi/L, which by definition is equal to 5 X 10^{-12} grams of radium per liter, they would still be soluble. Radium is an alkaline earth metal very similar to calcium and magnesium and would be expected to act like these metals. Therefore, the removal of radium during softening is probably due to coprecipitation which is defined by Laitinen[16] as a phenomenon where the main precipitate and the impurity come down together. In this case hardness is the main precipitate and radium is the impurity.

Results of two tests performed at the U.S. EPA[14] on lime softening are given in Table 24. The radium data, after dual media filtering, indicate that removal is pH dependent with 84 percent and 94 percent radium removals at pH 9.5 and 10.5 respectively. This agrees with the coprecipitation theory because a greater percentage of the hardness was also removed at the higher pH as shown in Table 24.

Lime softening depends on the use of lime and soda ash to change the soluble calcium and magnesium compounds into nearly insoluble compounds that are flocculated, settled, and filtered. Conditions for carrying out the precipitation of calcium and magnesium vary because different pH levels are needed for each - about pH 9.5 for maximum precipitation of calcium carbonate and pH 10.5 for maximum precipitation

Table 24. Results of Lime Softening Pilot Plant Tests for Radium-226 Removal From Well Water*[14]

				Average Raw Water Concentration		Percentage Radium Removed				Percentage Hardness Removed	
						Settled Water		Filtered Water		Filtered Water	
Test Number	Date Started	Length of Tests hr	pH of Treated Water	Radium-226 pCi/L	Hardness (as $CaCO_3$) mg/L	First Stage	Second Stage†	Dual Media	GAC††	Dual Media	GAC††
1§	8/4/75	102	9.5	4.34	246	79		84	84	57	57
2**	8/18/75	77	10.5	4.82	256	92	93	94	95	62	62

*Illinois groundwater containing naturally occurring radium-226

†Second settling stage followed recarbonation that lowered pH to 9.8.

††Filtrasorb 200, Calgon Corp., Pittsburgh, PA.

§Samples collected only on 8/8, 8/9, and 8/10

**Samples collected only on 8/20 and 8/21 of magnesium hydroxide. Hence, if magnesium concentration is low, treatment to a pH of 9.5 will be sufficient. If magnesium concentration is high, excess lime, to produce pH of 10.5 can be used. Soda ash is added as needed to precipitate noncarbonate hardness. Recarbonation is used to stabilize lime treated water, reducing its scale forming potential. Carbon dioxide neutralizes excess lime precipitating it as calcium carbonate. Further recarbonation converts carbonate to bicarbonate.

Results of radium and hardness removals at water treatment plants using lime soda ash softening are given in Table 25.[17] The table shows that radium removal varied from 75 to 96 percent and that lime soda softening is effective for removing radium. The Webster City plant was using lime only during August 1974 measurements, but was using soda ash during the February 1975 measurements. Table 25 shows an increase in radium and hardness removal and an increase in process pH during the February 1975 test. The data indicate that percent radium removal increases as pH increases and this is shown in Figure 40.[9]

DOW RADIUM SELECTIVE COMPLEXER[17, 18]

Background

The Radium Selective Complexer was invented by Professor M. J. Hatch, New Mexico Institute of Mining and Technology, Socorro, New Mexico. Professor Hatch was formerly an employee of Dow Chemical and he remains a consultant to the Dow Company.

The Radium Selective Complexer (RSC) was originally intended for removal of soluble radium from uranium mine waters. The mining industry currently uses barium sulfate precipitation for this purpose.

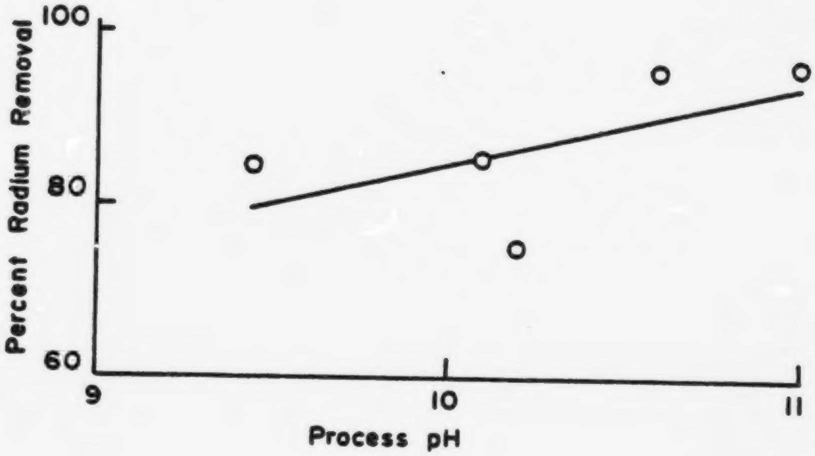

Figure 40. Percent radium removal as a function of pH during water softening[9]

Table 25. Ra-226 and Hardness Removals at Water Treatment Plants Using Lime-Soda Ash Softening[9]

City	Sampling Point	Ra-226		Hardness		pH of Process
		pCi/L	Percent Removal	mg/L	Percent Removal	
Elgin	Well	5.6		237		
	Filter Eff.	0.8	88	102	57	
Peru	Well	5.8		326		
	Filter Eff.	1.1	81	94	71	
Webster City (Aug. 1974)	Well	6.1		507		
	Clarifier #1 Eff.	1.9		333		10.0
	Clarifier #2 Eff.	2.6		282		10.1
	Filter Eff.	0.9	85	262	48	9.3
Webster City (Feb. 1975)	Well	7.8		482		
	Clarifier Eff.	0.6		150		11.0
	Filter Eff.	0.3	96	106	78	9.9
West Des Moines	Well	9.3		376		
	Contact Unit Eff.	2.6		215		10.1-10.4
	Filter Eff.	2.4	75	190	50	9.4-9.5

Several tests of the application of the RSC for removal of radium from these waters have been conducted and one of these studies is described by Boyce.[19] A large RSC installation is presently in operation for uranium mine waters at the Key Lake Mine/Mill in northern Saskatchewan.

A full scale trial was conducted in Bellville, Texas to demonstrate the RSC technology for drinking water treatment.[17] A full scale system was also installed for drinking water treatment in South Superior, Wyoming in November 1983 and operated for 13 months.[18] Several two inch diameter demonstration columns have also been pilot tested for long periods of time in Missouri and Iowa on potable water systems.

Results of testing demonstrated that the RSC selectively removed radium to concentrations below the MCL for extended lengths of time as long as iron fouling was eliminated. The investigators concluded that iron, if present, must be removed prior to treatment with the RSC system.

Test Results

Bellville, Texas[17] --

A full scale trial to demonstrate radium removal began at Bellville, Texas in February, 1983. Radium results are given in Table 26. The table shows that the RSC removed total radium from influent concentrations of 81 to 102.3 pCi/L to effluent concentrations of below the MCL for a period from February 2, 1983 to April 13, 1983. The RSC system was also tested at different loading rates given in Table 26 and indications were that the system can operate at a loading rate of up to 10 gpm/ft^2 with no reduced radium removal.

South Superior, Wyoming[18] --

A full scale RSC system was tested at South Superior Wyoming. A seven foot high by five foot diameter conventional water conditioning vessel was utilized for this system. The internal distributors were wrapped with 40 mesh screen to retain the RSC. The system was operated downflow at up to 10 gpm/ft^2 and was backwashed twice/week due to severe iron particulate problems. Effluent samples were taken every two weeks. Test results are given in Table 27. The RSC bed was a good filter for particulates which could not be completely removed by backwashing. This is partially due to resin density which only allows a backwash rate of 5 gpm/ft^2 compared to a downflow rate of 10 gpm/ft^2. The particulates are driven deep into the bed and aren't effectively removed. This system was operated successfully for eight (Table 27) months before particulate iron leakage through the bed carried radium into the effluent. The system averaged greater than 75% radium removal from November 3, 1983 to September 24, 1984, even though it was operating as an iron particulate removal system as well as a radium removal system.

Demonstration Columns[18] --

Demonstration columns that were 5 ft high X 2 in diameter, containing 4 ft depth of RSC were operated in St. Charles County, Missouri, Washington, Iowa, Eldon, Iowa, Holstein, Iowa and West Bend, Iowa. The 4 ft depth of RSC decreases to a 3 ft depth as it converts to the calcium form. These systems were operated down flow and backwashed only if particulate matter plugged the bed.

Particulate iron was a problem with the RSC system in St. Charles County, Missouri and conventional iron removal was required. Three of

TABLE 26. RADIUM REMOVAL CHRONOLOGY - BELLVILLE, TEXAS[17]

Date	Comments	Gross Alpha pci/L	Gross Beta pci/L	Ra 226 pci/L	Ra 228 pci/L
2/ 2/83	Well #6	86.0 ± 11.0	30.0 ± 4.0	91.0 ± 5.3	11.3 ± 2.5
2/ 2/83	System Start	< 2.0	< 3	< 0.6	< 1.0
2/ 3/83	Well #6	85.0 ± 10.0	28.0 ± 4.0	75.9 ± 8.0	7.6 ± 2.9
2/ 3/83	3.7 gpm/ft^2	< 2.0	< 3	< 0.6	< 1.0
2/ 7/83	Well #6	124.0 ± 13.0	28.0 ± 6.0	96.0 ± 5.0	5.3 ± 3.0
2/ 7/83	6.4 gpm/ft^2	< 2.0	< 3	< 0.6	< 1.0
2/ 8/83	7.4 gpm/ft^2	< 2.0	< 3	< 0.6	< 1.0
2/ 8/83	9.3 gpm/ft^2	< 2.0	< 3	< 0.6	< 1.0
2/ 9/83	10.0 gpm/ft^2	< 2.0	8.0 ± 4.0	< 0.6	< 1.0
2/17/83	Well #6	89.0 ± 8.0	23.0 ± 3.0	78.0 ± 3.0	3.0 ± 2.0
2/17/83	.5 mm gal (5.6 gpm/ft^2)	< 2.0	< 3	< 0.6	< 1.0
2/17/83	Texas Health Dept.	< 2.0	7.2 ± 3.0		
2/23/83	1.0 mm gal (5.5 gpm/ft^2)	< 2.0	10.0 ± 5.0	< 0.6	< 1.0
3/2/83	1.5 mm gal (5.7 gpm/ft^2)	< 2.0	4.0 ± 2.0	< 0.6	< 1.0
3/9/83	Start 24 hr/day oper.	< 2.0	< 3.0	< 0.6	< 1.0
3/16/83	4.5 mm gal (6 gpm/ft^2)	< 2.0	4.0 ± 2.0	< 0.6	< 1.0
3/16/83	Texas Health Dept.	3.7 ± 1.7	8.9 ± 3.2		
3/23/83	7.1 mm gal (6 gpm/ft^2)	< 2.0	< 3.0	< 0.6	< 1.0
3/30/83	9.6 mm gal (11 gpm/ft^2)	5.0 ± 3.0	4.0 ± 2.0	0.8 ± 0.5	< 1.0
4/6/83	12.0 mm gal (11 gpm/ft^2)	3.0 ± 2.0	5.0 ± 2.0	2.0 ± 0.5	< 1.0
4/13/83	14.4 mm gal (10.7 gpm/ft^2)	< 2.0	11.0 ± 3.0	< 2.0	< 1.0

TABLE 27. RADIOLOGICAL RESULTS FROM FULL SCALE SYSTEM SOUTH SUPERIOR, WYOMING[18]

Date	Sample Description	Gross Alpha pci/L	Gross Beta pci/L	RA226 pci/L	RA228 pci/L
6/24/83	Raw Water	15±5	19±4	20±1	0.0±4.2
7/11/83	Raw Water	26±5	26±4	11±1	2.2±2.5
7/27/83	Raw Water	34±2	20±1	16±1	0.0±2.4
8/08/83	Raw Water	8.9±3.7	17±3	12±1	2.5±3.4
8/24/83	Raw Water	24±2	15±1	13±1	0.9±1.3
9/08/83	Raw Water	28±4	26±3	13±1	1.8±1.4
11/3/83	Finished Water	3.6±1.1	9.1±1.1	3.9±1.2	1.1±2.1
12/12/83	Finished Water	2.2±0.8	20±1	0.1±0.1	1.4±1.3
12/19/83	Finished Water	5.1±1.0	20±1	0.1±0.1	0.0±1.9
12/27/83	Finished Water	1.2±0.9	16±1	2.2±0.4	0.0±1.8
1/03/84	Finished Water	16±3	15±2	3.0±0.4	0.0±1.7
1/09/84	Finished Water	5.1±2.7	13±2	2.5±0.4	1.6±3.6
1/17/84	Finished Water	7.5±1.9	15±2	1.0±0.4	0.0±1.8
1/23/84	Finished Water	8.8±1.4	15±1	2.9±0.4	2.0±1.4
2/06/84	Finished Water	6.6±2.0	14±2	2.7±0.4	0.0±1.6
2/21/84	Finished Water	10±3	34±2	2.1±0.4	0.0±1.0
3/05/84	Finished Water	7.3±2.5	12±2	1.4±0.3	0.0±2.1
3/19/84	Finished Water	16±3	15±2	2.9±0.5	0.5±0.6
4/03/84	Finished Water	16±4	12±2	6.5±1.0	0.0±2.4
4/16/84	Finished Water	8.0±2.2	13±2	3.8±0.9	2.6±2.8
4/30/84	Finished Water	0.7±2.2	11±4	0.5±0.1	0.0±1.3
5/14/84	Finished Water	5.3±2.4	8.8±1.7	0.9±0.2	0.0±1.2
5/29/84	Finished Water	4.1±2.0	9.9±1.5	1.6±0.3	0.9±1.1
6/11/84	Finished Water	5.2±3.0	11±2	1.3±0.3	1.4±1.2
6.18/84	Finished Water	4.0±3.0	8.9±2.4	3.8±0.6	0.8±1.3
7/02/84	Finished Water	1.1±2.2	14±2	4.0±0.5	0.7±2.5
7/16/84	Finished Water	8.8±3.6	16±3	5.3±0.8	3.1±2.2
7/30/84	Finished Water	6.5±4.2	12±3	3.9±0.8	1.3±3.6
8/13.84	Finished Water	3.4±3.8	4.7±2.9	11.4±0.9	0.0±1.8
8/27/84	Finished Water	3.0±3.1	15±3	6.2±1.0	1.5±2.7
9/10/84	Finished Water	14±4	19±3	10±1	3.9±3.3
9/17/84	Finished Water	11.5±5.2	6±1	6.3±0.6	0.8±2.3
9/24/84	Finished Water	7.1±3.5	15.6±2.7	11.7±1.0	2.1±2.5

Results by Core Laboratories, Inc., Casper, Wyoming the four systems in Iowa were located downstream of an existing iron removal system and upstream of water softeners (if they existed).

The RSC unit in Washington, Iowa operated for eleven months with greater than 90% radium removal. Iron was not a problem at this location and no iron removal treatment was used.

The RSC unit at Eldon, Iowa leaked radium after two months of operation because the iron removal system did not remove enough iron to prevent fouling of the RSC.

The RSC unit at Holstein, Iowa removed greater than 90% of the radium for a period of 8 months. This town had iron removal treatment that was adequate for the RSC system.

The RSC unit at West Bend, Iowa removed greater than 90% of the radium for a period of ten months. Adequate iron removal treatment was also in operation for this town.

In summary these results show that the RSC is satisfactory for radium removal if iron is kept from fouling the RSC system.

REVERSE OSMOSIS

Reverse Osmosis (RO) has been demonstrated to be an effective process for removal of radium from drinking water. Table 28 gives information on eight reverse osmosis systems in Sarasota County, Florida[20] that were tested for radium removal. The type and performance of the eight systems varied, but they all lowered the radium concentration below the MCL. The groundwater throughout Sarasota County, Florida is generally poor, containing high concentrations of hardness, sulfate, sodium, and chloride as well as Ra-226. Therefore, in addition to solving the radium problem the RO systems are producing a better overall quality of water. Another advantage of RO is that it requires a small space as compared to the space needed for conventional coagulation or lime softening. The principal disadvantage of RO is high operating cost because of high energy consumption, large quantity of reject water, and pretreatment requirements.

New low pressure (< 200 psi) membranes have been developed recently and they have been shown to remove greater than 95% of the divalent cations including radium. Low pressure membranes will reduce energy costs. Also new high pressure RO units that are well-maintained should give better than 98% radium removal.

ELECTRODIALYSIS REVERSAL[21]

Electrodialysis (ED) is an electrochemical separations process in which ions are transferred through membranes from a less concentrated to a more concentrated solution as a result of the flow of direct electric current. Electrodialysis Reversal (EDR) is a relatively recent development in which the polarity of the direct current is changed approximately every 15 minutes. A compartment which was formerly a demineralizing compartment becomes a concentrating compartment (and vice versa). It is necessary to switch valves which feed and collect these two streams shortly after the current is reversed. It is also necessary to divert both streams at the time of polarity reversal for a period of about one minute to purge both compartments before the demineralizing stream returns to making product water. The whole process is completely automatic.

EDR, therefore, is achieved by symetrical equal-time operation in alternating directions so that insoluble or sparingly-soluble substances which would otherwise coat the membranes will, during the reversed polarity period, tend to be removed.

TABLE 28. RADIUM REMOVAL BY RO IN SARASOTA COUNTY, FL.[20]

Location	Membrane Type	Operating Press (PSI)	Stages No.	Actual Recovery %	Ra-226(pCi/L) in	Ra-226(pCi/L) out	Removal %
Venice	Hollow Fiber	400	2	54	3.4	0.3	91.2
Sorrento Shores	Spiral Wound	425	1	39	4.6	0.2	95.7
Spanish Lakes	Spiral Wound	400	2	31	10.5	1.2	88.6
Bay Lakes Estates	Hollow Fiber	400	2	NA	3.2	0.1	96.9
Kings Gate	Hollow Fiber	400	2	NA	15.7	2.0	87.3
Sarasota Bay	Hollow Fiber	400	1	50	20.5	0.3	98.5
Bay Front	Hollow Fiber	200	1	28	12.1	0.6	95.0
Nokomis School	Spiral Wound	200	1	NA	11.1	0.5	95.5

An operating EDR unit requires a supply of pressurized feed water in the range of 70 to 90 psi, a reversing DC power supply, and an array of demineralization stages in a membrane stack or stacks. In order to conserve water, a concentrate recirculation pump is used to recirculate most of the water to the concentrating compartments. The actual waste concentrate flow is then simply regulated by a control valve in the feed line and forces an equal amount of water out to waste.

EDR is the only membrane process which is symmetrically reversible. Reversal inhibits the formation of scale and fouling films on the surface of membranes without addition of chemicals to the feed water, minimizes pretreatment, and maximizes recovery.

A major application of EDR is the demineralization of brackish waters of several thousand mg/L of salts to potable levels below 500 mg/L. The Florida waters, mentioned previously under reverse osmosis, that had high dissolved salts and radium would also be good candidates for EDR treatment. EDR systems have found great favor in remote locations and village water supply applications, where limited operator skills and availability of chemicals make other processes less attractive.

EDR systems remove about 40% of the dissolved salts per stage. Therefore, if the total radium concentration in the source water were 40 pCi/L, then five stages would probably be required to remove radium to a concentration below the MCL. The specific water analysis is important for individual cases because the rate of removal of individual ions will vary depending on such conditions as: water profile of ions, water temperature, total ion removal percentage, number of stages, water recovery rate and current density.

EDR systems are relatively expensive about the same as reverse osmosis, but they should be considered for small systems on brackish waters where little operator attention would be available.

POTASSIUM PERMANGANATE GREENSAND FILTRATION

The literature shows that radium was removed across $KMnO_4$ greensand processes; removal was variable; and the exact reasons for radium removal were not known.[8,9] After reviewing this earlier literature and the manganese dioxide results of the University of Iowa Study (Section 5) there are very strong indications that a properly controlled MnO_2-filtration process would do a fine job of removing radium.

Oxidation of Mn^{2+} ions occurring in natural waters and/or reduction of $KMnO_4$ leads to the formation of colloidal MMO_2.[22] This possesses a negative surface charge over the normal pH range in natural waters. Figures 20 through 23 show good sorption of radium by MnO_2 above pH 5. The high surface area of the colloidal MnO_2 along with the negative charge exerts a dominating influence on the concentration of many elements, e.g. the heavy metals, in the aquatic environment.[22]

Radium concentrations in water are normally in the 10^{-9} mg/L range. Iron, manganese and other cations that strongly compete with radium for adsorption sites on MnO_2 are present in the 10^{-1} mg/L concentration range. Therefore, in order to obtain good radium sorption, it would be necessary to remove as much of the competing cations as possible and reserve the sorption sites on MnO_2 for radium. This is possible by installing a good iron manganese removal process before the MnO_2 - filtration process or making sure that some MnO_2 is still available for radium sorption. When $KMnO_4$ is added during iron removal, Fe^{2+} is oxidized and precipitated as Fe^{3+}. The $KMnO_4$ is reduced to MnO_2 which is available for sorption of cations. Any Fe^{2+} that is still present will compete with radium for sorption sites on the MnO_2. Therefore, a final treatment stage consisting of stoichiometric Mn^{2+} oxidation with $KMnO_4$ to have MnO_2 available for radium adsorption and final filtration would be required for complete removal of radium.

This is verified by the data given in table 29. The table shows that the best radium removal was obtained at Hersher, IL. where Ra-226 removal ranged from 47 to 56 percent. It can be seen that the iron concentraion ranges from 0.1 to 0.4 mg/L and is relatively low compard to manganese concentration that ranges from 0.41 to 0.63 mg/L. Iron/manganese removal at Hersher consists of aeration, settling, chlorination, filtration and treated with polyphosphate and potassium permanganate.[23] This data strongly indicates that iron was removed and Mn^{2+} was oxidized to MnO_2, $KMnO_4$ was also reduced to MnO_2 and, therefore, sorption sites on the MnO_2 were available for radium removal.

Some selected data, furnished by the State of Virginia Department of Health in Danville, VA, and presented in table 30, show that three treatment systems utilizing continuous feed $KMnO_4$, 30-minute contact time, and manganese greensand all removed radium to concentrations below the MCL. This data shows that the $KMnO_4$ - greensand processes can be operated for optimum radium removal.

TABLE 29. RADIUM-226, IRON, AND MANGANESE REMOVALS BY IRON- AND MANGANESE-REMOVAL PROCESSES[23]

City	Raw Water pH	Ra-226 Raw Water pCi/L	Ra-226 Treated Water pCi/L	Ra-226 Removal per cent	Iron Raw Water mg/L	Iron Treated Water mg/L	Iron Removal per cent	Manganese Raw Water mg/L	Manganese Treated Water mg/L	Manganese Removal per cent
Adair, IA	6.7-6.9	13	8	38	1.1	0.02	98	0.01	0.01	-
Eldon, IA	7.8	49	43	12	2.0	0.3	85	0.01	0.01	-
Estherville, IA	7.7	5.7	5.1	11	2.0	0.67	66	0.24	0.27	-
Grinnell, IA	7.6	6.7	5.7	15	0.7	0.41	42	0.01	0.01	-
Herscher, IL	7.6-8.3	14.9	6.6	56	0.2	0	-	0.47	0.02	96
	7.6-8.3	14.5	6.4	56	0.4	0	-	0.41	0.01	98
	7.6-8.3	14.9	6.9	54	0.1	0	-	0.48	0.01	98
	7.6-8.3	14.3	6.9	42	0.1	0	-	0.39	0	100
	7.6-8.3	14.0	6.9	51	0.1	0	-	0.45	0	100
	7.6-8.3	13.9	6.8	51	0.1	0	-	0.63	0	100
	7.6-8.3	13.9	7.3	47	0.2	0.1	-	0.44	0.13	70
	7.6-8.3	14.1	6.3	55	0.1	0	-	0.53	0.02	96
	7.6-8.3	14.3	6.5	55	0.1	0	-	0.50	0	100
Holstein, IA	7.4-7.6	13	7	46	1.8	0.09	95	0.15	0.01	93
Stuart, IA	7.6-7.9	16	12	25	0.94	0.03	97	0.01	0.01	-

TABLE 30. RADIUM REMOVAL WITH THE $KMnO_4$ - GREENSAND PROCESS†

Location	Description	Gross x pCi/L	Ra-226 pCi/L	Ra-228 pCi/L	Total Ra pCi/L
#1	influent	6.8	3.7	3.3	7.0
	effluent	1.5	0.6	0.0	0.6
#2	influent	22.3	10.7	10.8	21.5
	effluent	3.9	0.5	0.5	1.0
#3	influent	6.2	5.3	5.9	11.2
	effluent	0.6	0.9	1.4	2.3

† Information provided by State of Virginia Department of Health, Danville, VA.

SECTION 9

COSTS

For many communities, a specific process would be selected because it is desirable to remove radium along with other dissolved solids. For example, if the water supply has high hardness, then ion exchange or lime softening would be selected to remove both radium and hardness. A community that has a brackish water supply with radium would select reverse osmosis or electrodialysis. If the water supply is of excellent quality, except for radium, then the RSC, calcium cation exchange or $KMnO_4$ with filtration may be selected. Calcium cation exchange and $KMnO_4$ with filtration have never been used exclusively for radium removal and pilot testing would be required before full scale installation. If $KMnO_4$ with filtration is used on water of otherwise excellent quality, then it would be necessary to add manganous ion and the oxidation of the manganous ion and reduction of $KMnO_4$ would form the MnO_2 that is necessary to sorb radium. Only a small quantity of manganous ion (about one mg/L) and $KMnO_4$ added stoichiometrically is all that would be required for water that has a low concentration of dissolved solids. The spent MnO_2 would precipitate on the filter. Water supplies frequently contain both iron and hardness, in which case both iron and hardness removal processes would be required. It was shown in section 5 that conventional iron removal consisting of aeration and filtration would not be expected to remove more than 10 to 20% of the radium present. There are possibilities for optimizing an iron removal process such as backwashing the sand with dilute acid or adding extra $KMnO_4$ for better radium removal. These modifications to the iron removal process would be specific to a water supply and pilot testing of the modification on each specific water supply should be performed before full scale application.

The use of the RSC discussed in section 7 of this report is an example of a possible cost savings. In this case the RSC was used to treat the waste brine instead of the entire water supply. Therefore, a much smaller quantity of complexer (5 ft^3 instead of 30 ft^3) and a smaller reaction vessel was required. This approach will also involve a smaller quantity of complexer with easier handling for final disposal.

Table 26, compiled from the literature,[24,25,26] compares approximate costs of the different processes for removing radium. The table does not include disposal costs. As mentioned, each specific water supply that needs radium removal should be considered separately. Objective pilot testing on each water supply would be required to select the most economical process or processes for that water source.

TABLE 26. ESTIMATED COSTS OF RADIUM REMOVAL PROCESSES[24, 25, *]

	100,000 gal/day			500,000 gal/day		
Process	const. $	O&M $/yr.	Total $/1000 gal.	const. $	O&M $/yr.	Total $/1000 gal
Ion Exchange+	99,900	17,100	0.80	164,100	27,100	0.26
Lime Soda Softening#	121,200	16,900	0.85	200,200	24,200	0.26
Iron & Manganese†	157,000	9,500	0.76	274,000	21,700	0.30
Reverse Osmosis§	194,900	43,600	1.82	684,900	169,400	1.37
Electro-dialysis**	221,300	36,900	1.74	737,600	158,100	1.36
Dow Complexer++	99,900	5,700	0.48	164,100	9,000	0.15
$KMnO_4$ with Filtration##	122,800	10,000	0.66	212,700	19,900	0.24

* Costs brought up to 1986 with ENR index.[26] Capital cost amortized at 10% for 20 yrs. Waste disposal costs not included, pretreatment and post treatment costs not included.

+ For strong acid ion exchange resin.

# Single stage

† Spray aeration plus pressure sand filtration, chlorine, $KMnO_4$ and polymer included.

§ For 2000 mg/L TDS, low pressure membrane.

** For 2000 mg/L TDS

++ Used ion exchange construction cost and 1/3 of O&M cost.

## $KMnO_4$ feed system to form MnO_2 followed by pressure sand filtration.

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